

METHOD FOR CLEANING EXHAUST AND APPARATUS THEREFOR

Publication number: JP2002361047 (A) **Also published as:**
Publication date: 2002-12-17 **JP4174976 (B2)**
Inventor(s): AKAMA HIROSHI; HANAKI YASUNARI;
KAMIJO MOTOHISA + (AKAMA HIROSHI, ;
HANAKI YASUNARI, ; KAMIJO MOTOHISA)
Applicant(s): NISSAN MOTOR + (NISSAN MOTOR CO LTD)
Classification:
- **international:** B01D39/14; B01D39/20; B01D46/00;
B01D46/42; B01D53/86; B01D53/94;
B01J23/42; B01J23/89; B01J29/74;
B01J35/06; F01N3/02; F01N3/08; F01N3/10;
F01N3/24; F01N3/28; B01D39/14; B01D39/20;
B01D46/00; B01D46/42; B01D53/86;
B01D53/94; B01J23/42; B01J23/89;
B01J29/00; B01J35/00; F01N3/02; F01N3/08;
F01N3/10; F01N3/24; F01N3/28; (IPC1-
7): B01D39/14; B01D39/20; B01D46/00;
B01D46/42; B01D53/86; B01D53/94;
B01J23/42; B01J23/89; B01J29/74; B01J35/06;
F01N3/02; F01N3/08; F01N3/10; F01N3/24;
F01N3/28
- **European:**
Application number: JP20010167506 20010601
Priority number(s): JP20010167506 20010601

Abstract of JP 2002361047 (A)

PROBLEM TO BE SOLVED: To provide a method for cleaning exhaust by which NOx and PM can be continuously self-removed under ordinary burning conditions without requiring specified control and to provide an exhaust cleaning catalyst and an apparatus for cleaning exhaust. **SOLUTION:** In the method for cleaning exhaust, PM particles and NOx in exhaust are removed by converting the PM particles to HC by a reaction represented by the formula $mC + nH_2O \rightarrow H_2nCm + n/2O_2$. The apparatus for cleaning exhaust has a filter obtained by carrying a noble metal and fine oxide particles of $\leq 1 \mu m$ average particle diameter on the inner walls of pores in a monolithic filter and disposed in an exhaust flue. In the method for cleaning exhaust, hydrogen generation reactions represented by the formulae $C + H_2O \rightarrow H_2 + CO$ and $C + 2H_2O \rightarrow 2H_2 + CO_2$ are carried out at ≤ 500 deg.C exhaust temperature.; The exhaust cleaning catalyst contains an H₂ generation catalyst and an NO_x removal catalyst, the H₂ generation catalyst contains Rh-carrying porous particles and metals such as Fe, Co, Mn and Ni, and these metals are contained at a ratio of 0.1-10 when Rh is represented by 1.

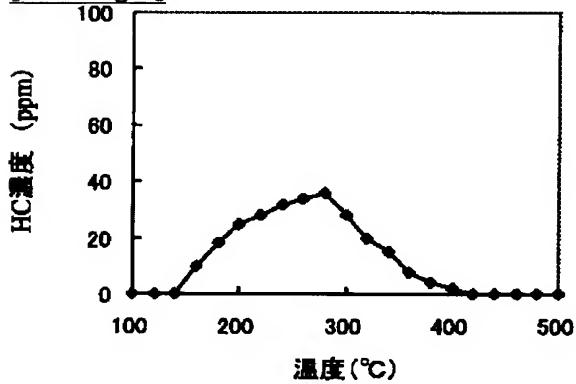
* NOTICES *

JPO and INPIT are not responsible for any damages caused by the use of this translation.

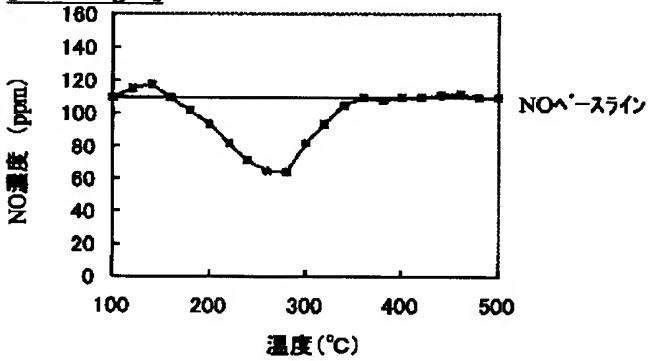
1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. **** shows the word which can not be translated.
3. In the drawings, any words are not translated.

DRAWINGS

[Drawing 1]

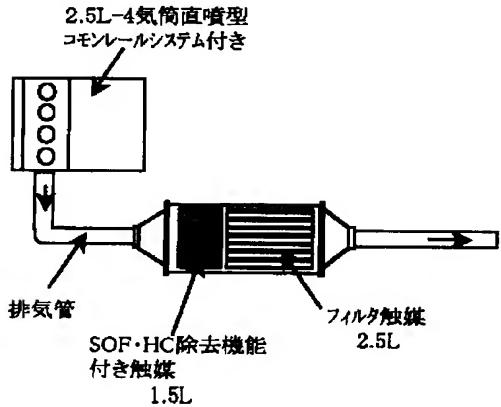


[Drawing 2]

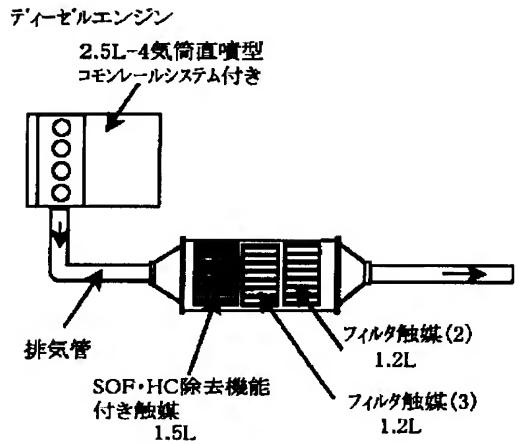


[Drawing 3]

ディーゼルエンジン



[Drawing 4]



[Translation done.]

*** NOTICES ***

JP0 and INPIT are not responsible for any damages caused by the use of this translation.

- 1.This document has been translated by computer. So the translation may not reflect the original precisely.
- 2.**** shows the word which can not be translated.
- 3.In the drawings, any words are not translated.

CLAIMS**[Claim(s)]**

[Claim 1]It is how to purify particulate particles and nitrogen oxides under exhaust air, and they are next reaction-formula 1 $mC + nH_2O \rightarrow H_{2n}C_m + n/2$, and O_2 . -- (1)

An exhaust-air-purification method including a process in which come out and particulate particles are changed into hydrocarbon by the reaction expressed.

[Claim 2]making the above-mentioned hydrocarbon react to nitrogen oxides -- the following reaction-formula $2H_{2n}C_m + 4NO \rightarrow 2N_2 + mCO_2 + nH_2O$ -- (2)

An exhaust-air-purification method according to claim 1 including a process out of which it comes and which is changed into nitrogen, carbon dioxide, and water by the reaction expressed.

[Claim 3]An exhaust-air-purification method according to claim 1 or 2 performing a reaction expressed with the above-mentioned reaction formula 1 at temperature of 350 ** or less.

[Claim 4]An exhaust-air-purification method according to claim 3 performing a reaction expressed with the above-mentioned reaction formula 1 at temperature of 280 ** or less.

[Claim 5]An exhaust-air-purification method given in any one paragraph of the Claims 1-4 performing a reaction expressed with the above-mentioned reaction formula 2 at temperature of 350 ** or less.

[Claim 6]An exhaust-air-purification method according to claim 5 performing a reaction expressed with the above-mentioned reaction formula 2 at temperature of 280 ** or less.

[Claim 7]It is a device which purifies particulate particles and nitrogen oxides under exhaust air using an exhaust-air-purification method of a description in any one paragraph of the Claims 1-6, At least one sort of noble metal components chosen from a group which changes from platinum, palladium, and rhodium to a pore inside wall of a monolith type filter, An exhaust emission control device allocating in an engine smoke way of an internal-combustion engine a filter with a catalyst function which supports at least one sort of oxide particles chosen from a group which comprises alumina, a titania, zirconia, and silica whose mean particle diameter is 1 micrometer or less.

[Claim 8]The exhaust emission control device according to claim 7, wherein mean particle diameter of the above-mentioned oxide particles is 0.6 micrometer or less.

[Claim 9]The exhaust emission control device according to claim 7 or 8, wherein porosity of the above-mentioned monolith type filter is 30 to 80% and an average pore diameter is 5-40 micrometers.

[Claim 10]An exhaust emission control device given in any one paragraph of the Claims 7-9, wherein a filter with the above-mentioned catalyst function is divided into two or more steps, is arranged in series and changes.

[Claim 11]The exhaust emission control device according to claim 10 in which pressure loss of a filter with a catalyst function of the exhaust air upstream is characterized by being larger than pressure loss of a filter with a catalyst function of the exhaust air downstream.

[Claim 12]The exhaust emission control device according to claim 10 or 11 in which an average pore diameter of a filter with a catalyst function of the exhaust air upstream is characterized by being larger than an average pore diameter of a filter with a catalyst function of the exhaust air downstream.

[Claim 13]An exhaust emission control device given in any one paragraph of the Claims 10–12 to which porosity of a filter with a catalyst function of the exhaust air upstream is characterized by being larger than porosity of a filter with a catalyst function of the exhaust air downstream.

[Claim 14]An exhaust emission control device given in any one paragraph of the Claims 10–13, wherein a filter with a catalyst function of the above-mentioned exhaust air upstream has a collision filtration function.

[Claim 15]An exhaust emission control device given in any one paragraph of the Claims 10–14, wherein a filter with a catalyst function of the above-mentioned exhaust air downstream has a surface filtration function.

[Claim 16]An exhaust emission control device given in any one paragraph of the Claims 10–15 which a filter with a catalyst function of the above-mentioned exhaust air upstream uses textile fabrics and/or a nonwoven fabric of ceramic fiber, and are characterized by things.

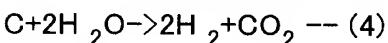
[Claim 17]An exhaust emission control device given in any one paragraph of the Claims 10–16 which a filter with a catalyst function of the above-mentioned exhaust air downstream uses a ceramic sintered body, and are characterized by things.

[Claim 18]An exhaust emission control device given in any one paragraph of the Claims 10–17 which allocate in the exhaust air upstream of a filter with the above-mentioned catalyst function HC-SOF removal material which has the function to remove hydrocarbon and a soluble organic component, and are characterized by things.

[Claim 19]The exhaust emission control device according to claim 18 being at least one sort of zeolite and/or a silica content inorganic substance which were chosen from silica whose above-mentioned HC-SOF removal materials are mordenite, MFI, and beta type zeolite, and whose average pore size is 1–5 nm, and a group which comprises a laminar clay mineral.

[Claim 20]A manufacturing method of an exhaust emission control device characterized by making the above-mentioned noble metal component support with the impregnating method and/or plating after being the method of manufacturing an exhaust emission control device of a description in any one paragraph of the Claims 7–19 and making a pore inside wall of the above-mentioned monolith type filter carry out distributed support of the above-mentioned oxide particles.

[Claim 21]When it is how to purify particulate particles and nitrogen oxides under exhaust air and temperature of exhaust air discharged from an internal-combustion engine is 500 ** or less, they are the following reaction formula 3 and/or 4 C+H₂O→H₂+CO. -- (3)



An exhaust-air-purification method including a process in which come out and a hydrogen generating reaction expressed is performed.

[Claim 22]Powder of porosity particles in which it is an exhaust purification catalyst including a hydrogen producing catalyst and a nitrogen-oxides purifying catalyst which are used for an exhaust-air-purification method according to claim 21, and the above-mentioned hydrogen producing catalyst supported rhodium at least, An exhaust purification catalyst when rhodium is set to 1 including at least one sort of metal chosen from a group which comprises iron, cobalt, manganese, and nickel, wherein these metal is contained by a ratio of 0.1–10.

[Claim 23]The exhaust purification catalyst according to claim 22, wherein mean particle diameter of the above-mentioned porosity particles is 0.1–20 micrometers.

[Claim 24]An exhaust emission control device which is a device which purifies particulate particles and nitrogen oxides under exhaust air using the exhaust purification catalyst according to claim 22 or 23, allocates the above-mentioned hydrogen producing catalyst in the upstream of an engine smoke way of an internal-combustion engine, allocates the above-mentioned nitrogen-oxides purifying catalyst in the downstream, and is characterized by things.

[Claim 25]An exhaust emission control device which is a device which purifies particulate particles and nitrogen oxides under exhaust air using the exhaust purification catalyst according to claim 22 or 23, allocates a layered product of the above-mentioned nitrogen-oxides purifying catalyst in engine smoke Michigami of an internal-combustion engine, covers the above-mentioned hydrogen producing catalyst on it, and is characterized by things.

[Translation done.]

*** NOTICES ***

JP0 and INPIT are not responsible for any damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.
- 2.**** shows the word which can not be translated.
3. In the drawings, any words are not translated.

DETAILED DESCRIPTION**[Detailed Description of the Invention]****[0001]**

[Field of the Invention] This invention relates to the exhaust-air-purification method, an exhaust purification catalyst, and an exhaust emission control device, and, more particularly, relates to the exhaust-air-purification method, exhaust purification catalyst, and exhaust emission control device which are efficient and can purify the particulate (PM) particles and nitrogen oxides (NOx) under exhaust air generated from an internal-combustion engine etc.

[0002]

[Description of the Prior Art] In recent years, the lean burn engine operated also with an air-fuel ratio higher than theoretical air fuel ratio from a viewpoint of fuel consumption improvement and reduction of carbon-dioxide emissions is spreading. Especially the diesel power plant attracts attention anew from because of that of the low fuel consumption.

[0003] However, since the exhaust-gas temperature is low during exhaust air, including PM which is a part for a particle, with the catalyst of a conventional type, efficient exhaust air purification is in a difficult situation. engine fuel-consumption-improvement art is markedly alike, and progresses these days, and since an exhaust-gas temperature is in the tendency to fall further, purification of exhaust air is becoming increasingly difficult.

An effective method of carrying out the efficient purification of the detrimental constituent under exhaust air of a diesel power plant is desired.

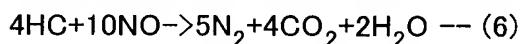
Although the oxidation catalyst which supports platinum (Pt) into fireproof high surface area inorganic carrier materials, such as alumina ($\text{aluminum}_2\text{O}_3$), is used as a catalyst for exhaust air purification of the conventional diesel power plant, Oxidation of CO and HC is a main function, and although the grade which a part for SOF also has can oxidize, effect is not shown in purification of the dry soot (C= carbon particle) which is the main ingredients of PM.

[0004] In order to purify the exhaust air which contains a part for PM like exhaust air of a diesel power plant, filtering technique is indispensable and many porous sintered bodies and fibrous filters which comprise cordierite and silicon carbide are proposed. As a raw material of the above-mentioned fibrous filter, what consists of various materials, such as alumina and silica, is proposed. Society of Automotive Engineers of Japan Although the diesel particulate filter (DPF) which used silicon carbide fiber is proposed by before [an academic lecture meeting] ** collection No.103-98 (1998 autumn conventions), The heater for removing PM which carried out the trap and reproducing a filter is indispensable, and since the complicated system is required, application is difficult for a passenger car with few mount spaces.

[0005] NO under exhaust air is converted into strong NO_2 of oxidizing power by arranging Pt system catalyst in the preceding paragraph of a filter as a method of reproducing a filter without using a heater, The oxidizing power of this NO_2 is used. A part for PM which carried out the trap to the filter. The method of burning is proposed ("Effects on after-treatment on particulate matter when JP,H1-318715,A, J.P.Warren, et.al.), using the Continuously Regenerating Trap" and ImechE. 1998 S491/006, B.Carberry, et.al., "A focus on current and future particle after-treatment systems", ImechE1998 S491/007. This method is a thing using the reaction of the

ingredients under exhaust air, and since the combustion purification of the part for PM which carried out the trap can be carried out continuously, it is called the continuous reproduction type trap. However, in order to burn C which was comparatively late as for the reaction velocity with NO_2 , and was discharged from the engine since the carbon (C) in PM was a particle at sufficient speed. It is necessary that the conditions of exhaust air require not less than 400 ** comparatively high temperature conditions, and to increase the amount of NO_2 which serves as an oxidizer in still such a temperature region. That is, in order to purify NO_x whose it was necessary to increase the NO_x emission from an engine and which increased as a result, a highly efficient NO_x catalyst is needed.

[0006]The various methods for purifying PM and NO_x simultaneously are also proposed. For example, to JP,H7-116519,A. The exhaust gas cleaning material which supports the catalyst which has a perovskite structure in a porous filter is proposed. It makes the particle-like substance and/or hydrocarbon which are contained in exhaust gas act as a reducing agent, this is how to return the nitrogen oxides under exhaust air, and it uses this catalyst, and is the following reaction formula 5 and $6\text{C}+2\text{NO} \rightarrow \text{N}_2+\text{CO}_2$. -- (5)



It is supposed that it comes out and NO_x is returned by the reaction expressed. In the above-mentioned reaction, since the reaction formula 6 is a reaction of gas molecules, it is difficult for expecting a catalysis to a catalysis being expected, since the reaction formula 5 is a reaction of a solid and a gas, and it is unknown whether filter regeneration is possible under the usual running mode conditions.

[0007]On the other hand, arranging a NO_x absorbent and a filter in the position in which heat transfer is possible, and burning PM after NO_x emission reduction from a NO_x absorbent is proposed by the patent printing No. 2722987 gazette. A NO_x absorbent is supported inside the septum stoma of a wall flow type filter, and the catalyst which unified the filter and the NO_x absorbent is proposed by JP,H9-94434,A.

[0008]These are art acquired combining the catalyst and filter which process NO_x , and need respectively different engine control for NO_x processing and PM combustion. In order to use a NO_x absorbent, to absorb NO_x and to return, the control which changes the air-fuel ratio (A/F) of exhaust air is required. For combustion of deposition PM for reproducing a filter, and removal of a sulfur compound by which the trap was carried out to the NO_x absorbent. It is required to perform reproduction of a filter on oxidizing atmosphere conditions to carrying out temperature up of a NO_x absorbent and/or the filter even more than 600 ** or it, and also performing removal of the sulfur compound from a NO_x absorbent under reducing atmosphere. Degradation of a catalyst is promoted by a temperature rise and there is a problem of high-cost-izing also systematically again. Control of such an exhaust-gas temperature or atmosphere (A/F) is complicated, and it is continuously anxious for the exhaust-air-purification method in which self-consecration is possible, without adding specific control under the usual travel condition from being accompanied by the sacrifice of fuel consumption or operability. Although the proposal which supports a catalyst in a filter was made for the purpose of simultaneous removal of PM and NO_x , the contact with a catalyst component and PM particles or the device from a viewpoint of probability of collision had not got used.

[0009]The place which this invention is made in view of SUBJECT which such ***** has, and is made into the purpose, It is in providing the exhaust-air-purification method which can carry out self-consecration of NO_x and the PM continuously without needing specific control under the usual burning conditions, an exhaust purification catalyst, and an exhaust emission control device.

[0010]

[Means for Solving the Problem]As a result of repeating examination wholeheartedly that this invention persons should solve an aforementioned problem, C particle (particulate particles) in PM is once changed into hydrocarbon or hydrogen, By raising a contact (collision) rate of a catalyst component and PM particles, and promoting this conversion reaction, it finds out that an

aforementioned problem is solvable and came to complete this invention.

[0011]Namely, an exhaust-air-purification method of this invention is how to purify particulate particles and nitrogen oxides under exhaust air, and are next reaction-formula 1 $mC+nH_2O \rightarrow H_{2n}C_m + n/2$, and O_2 . -- (1)

A process in which come out and particulate particles are changed into hydrocarbon by the reaction expressed is included.

[0012]The above-mentioned hydrocarbon is made to react to nitrogen oxides, and a suitable gestalt of an exhaust-air-purification method of this invention is the following reaction-formula $2H_{2n}C_m + 4NO \rightarrow 2N_2 + mCO_2 + nH_2O$. -- (2)

A process out of which it comes and which is changed into nitrogen, carbon dioxide, and water by the reaction expressed is included.

[0013]An exhaust emission control device of this invention is a device which purifies particulate particles and nitrogen oxides under exhaust air using an above-mentioned exhaust-air-purification method. At least one sort of noble metal components chosen from a group which changes from platinum, palladium, and rhodium to a pore inside wall of a monolith type filter. Mean particle diameter allocated in an engine smoke way of an internal-combustion engine a filter with a catalyst function which supports at least one sort of oxide particles chosen from a group which comprises alumina, a titania, zirconia, and silica which are 1 micrometer or less.

[0014]Porosity of the above-mentioned monolith type filter is 30 to 80%, and a suitable gestalt of an exhaust emission control device of this invention is characterized by an average pore diameter being 5-40 micrometers again.

[0015]A filter with the above-mentioned catalyst function is divided into two or more steps, and other suitable gestalten of an exhaust emission control device of this invention are arranged in series, and change.

[0016]A suitable gestalt of further others of an exhaust emission control device of this invention allocates in the exhaust air upstream of a filter with the above-mentioned catalyst function HC-SOF removal material which has the function to remove hydrocarbon and a soluble organic component.

[0017]After a manufacturing method of an exhaust emission control device of this invention being a method of manufacturing the above-mentioned exhaust emission control device and making a pore inside wall of the above-mentioned monolith type filter carry out distributed support of the above-mentioned oxide particles, the above-mentioned noble metal component is made to support with the impregnating method and/or plating again.

[0018]Other exhaust-air-purification methods of this invention are the following reaction formula 3 and/or 4 $C + H_2O \rightarrow H_2 + CO$, when it is how to purify particulate particles and nitrogen oxides under exhaust air and temperature of exhaust air discharged from an internal-combustion engine is 500 ** or less. -- (3)

$C + 2H_2O \rightarrow 2H_2 + CO_2$ -- (4)

A process in which come out and a hydrogen generating reaction expressed is performed is included.

[0019]Powder of porosity particles in which an exhaust purification catalyst of this invention is an exhaust purification catalyst including a hydrogen producing catalyst and a nitrogen-oxides purifying catalyst which are used for an above-mentioned exhaust-air-purification method, and the above-mentioned hydrogen producing catalyst supported rhodium at least, Including at least one sort of metal chosen from a group which comprises iron, cobalt, manganese, and nickel, these metal is contained by a ratio of 0.1-10, when rhodium is set to 1.

[0020]Other exhaust emission control devices of this invention are devices which purify particulate particles and nitrogen oxides under exhaust air using the above-mentioned exhaust purification catalyst again, The above-mentioned hydrogen producing catalyst is allocated in the upstream of an engine smoke way of an internal-combustion engine, and the above-mentioned nitrogen-oxides purifying catalyst is allocated in the downstream.

[0021]An exhaust emission control device of further others of this invention is a device which

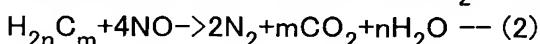
purifies particulate particles and nitrogen oxides under exhaust air using the above-mentioned exhaust purification catalyst, allocates a layered product of the above-mentioned nitrogen-oxides purifying catalyst in engine smoke Michami of an internal-combustion engine, and covers the above-mentioned hydrogen producing catalyst on it.

[0022]

[Embodiment of the Invention]Hereafter, the exhaust-air-purification method of this invention is explained in detail. Mass percentage is shown unless it mentions specially "%" in this Description.

[0023]By being the method of purifying the particulate (PM) particles and nitrogen oxides (NOx) under exhaust air, and changing PM particles into hydrocarbon (HC), by the usual travel condition, the exhaust-air-purification method of this invention is efficient, and purifies PM particles under exhaust air which does not burn easily. NOx is changed into harmless nitrogen (N₂), CO₂, and H₂O by making it react to NOx while exhausting generated HC. Generated HC may oxidize promptly and may be changed into carbon dioxide (CO₂) or water (H₂O).

[0024]That is, by the exhaust-air-purification method of this invention, they are the following reaction formula 1, and 2 mC+nH₂O→H_{2n}C_m+n/2 and O₂. -- (1)



NOx and PM are removed almost simultaneous by coming out and advancing the conversion reaction expressed. Although the details of the mechanism changed into HC have unknown C in PM at present in HC generation reaction (formula 1) by C and H₂O here, This invention persons performed evaluation which made Pt / alumina system catalyst react to the model gas of a C (graphite)/O₂/H₂O/N₂ system, for example, and as shown in the graph of drawing 1, they detected HC. As it evaluated by carrying out additional introduction of the NO into model gas and was shown in drawing 2, it checked that NO concentration decreased. Therefore, it can guess that HC generation reaction (formula 1) and the HC-NO reaction (formula 2) have occurred.

[0025]In order to advance the above-mentioned HC generation reaction (formula 1) and a HC-NO reaction (formula 2), it is preferred that temperature conditions shall be 350 ** or less, and it is more preferred to consider it especially as 280 ** or less so that the graph of drawing 1 which is an example, and drawing 2 may also show. Although lower limit temperature changes with performances of a catalyst, etc., if it is not less than 200 ** in temperature in general, remarkable reaction velocity will be obtained. Here, according to temperature conditions higher than 350 **, it is thought that oxidation reaction of HC generated by the above-mentioned HC generation reaction (formula 1) becomes superior, and it becomes inferior in strength [the above-mentioned HC-NO reaction (formula 2)]. It is known that the HC-NOx reaction (formula 2) on Pt system catalyst on exhaust air conditions with much oxygen (lean burn engine etc.) will advance notably in general on the other hand in a temperature region (150 ** – 300 **). Thus, since the above-mentioned HC generation reaction (formula 1) and a HC-NO reaction (formula 2) may be comparatively advanced by a low temperature service if the exhaust-air-purification method of this invention is used, without performing specific engine control, PM is efficient and can purify the exhaust air from the diesel power plant which poses a serious problem.

[0026]Next, the exhaust emission control device of this invention is explained in detail. In order to have advanced above-mentioned HC generation reaction (formula 1) and the above-mentioned HC-NO reaction (formula 2), it was an indispensable condition to use a catalyst, but this invention persons did the knowledge of it being very effective that a catalyst and PM particles carry out direct contact at this reaction. For example, the above-mentioned HC generation reaction (formula 1) advances, only when Pt / alumina system catalyst powder, and carbon (C) powder are mixed well enough, and when mixing is insufficient, it does not advance. The exhaust emission control device of this invention uses a filtration function positively as a means which raises the contact (collision) probability of a catalyst component and PM particles from this viewpoint. That is, it is considered as the exhaust emission control device which has a filtration function and a catalyst function, and the contact (collision) probability of PM particles and the catalyst component which flow in a narrow stoma by making a catalyst component

distribute and support on the pore inside wall surface of a filter is raised. As the support method of the above-mentioned catalyst component, the support method which covers the wall whole surface with plating etc. is effective so that it may mention later.

[0027]Here, the exhaust emission control device of this invention makes the pore inside wall of a monolith type filter support platinum (Pt), palladium (Pd) or (Rh), and the noble metal component that comprises these arbitrary combination as the above-mentioned catalyst component, and, specifically, grows into it. When it is not necessary to use a noble metal component in particular alone and is used combining two or more ingredients at this time, the above-mentioned HC generation reaction (formula 1) and a HC-NO reaction (formula 2) can be advanced more smoothly. For example, in the combination of Pt and Rh, HC generation reaction (formula 1) can be promoted by Pt, and a HC-NO reaction (formula 2) can be promoted by Rh.

[0028]To the pore inside wall of the above-mentioned monolith type filter. Mean particle diameter on the oxide particle of fines of 1 micrometer or less, and a concrete target. The alumina ($\text{aluminum}_2\text{O}_3$) used from the former as a carrier of a noble metal component, a titania (TiO_2), zirconia (ZrO_2) or silica (SiO_2), and the oxide particles concerning these arbitrary combination are made to support. From this, a stoma is not blockaded but a catalyst component distributes good on the surface of a pore inside wall. As for the above-mentioned mean particle diameter, it is more preferred that it is 0.6 micrometer or less. Even if the above-mentioned oxide particles are independent, it can be used, but when supporting two or more sorts of catalyst components and it is used combining two or more sorts of oxide particles, there is a more effective thing again. If mean particle diameter exceeds 1 micrometer, the stoma of the above-mentioned monolith type filter may be blockaded. The above-mentioned oxide particles can make the solution of hydroxide and the nitrate which can generate these oxide particles able to permeate the pore inside wall of a filter, and can carry out distributed support.

[0029]As the support method of the above-mentioned noble metal component or oxide particles, The method of making a filter pore inside wall carrying out osmosis support of the powder of oxide particles, and subsequently making a noble metal component supporting, the method of making a filter pore inside wall carry out immersion support of these oxide particles, after making oxide particles support a noble metal component beforehand, etc. can be illustrated. The former is more effective in order to expose a noble metal component to the particle surface side as much as possible especially.

[0030]As a carrier of the above-mentioned noble metal component or oxide particles, the filter of the monolith type which has a filtration function is used again. As for this monolith type filter, at this time, it is desirable for the basic characteristic as a filter to be excellent, i.e., they are high collection efficiency, quantity collection volume, and low pressure loss. It is good to be able to support a catalyst component (noble metal component) on the pore inside wall surface, and to make it contact with PM particles in which this catalyst component is under exhaust air, and high probability.

[0031]In the above-mentioned monolith type filter, it is preferred for porosity that it is 30 to 80%. When porosity is less than 30%, the large filter size for filling predetermined performance must be taken, and loadability may get worse. When it exceeds 80%, intensity may fall and loadability may get worse. It is preferred for a pore diameter that it is 5-40 micrometers in an average pore diameter. At this time, it is suitable for the particle diameter of the catalyst component which the size of a stoma supports, and since invasion of PM particles is attained easily and they can increase contact probability with a cell wall, it is effective. If smaller than 5 micrometers, even if invasion of PM particles will become difficult and it will invade, it may be hard to move in the inside of a stoma. On the other hand, when larger than 40 micrometers, the contact probability of PM particles and a cell wall will fall, and will pass through the inside of a stoma, without reacting.

[0032]As the above-mentioned monolith type filter, ceramic sintered bodies, such as cordierite, mullite, and SiC, textile fabrics, a nonwoven fabric of ceramic fiber (fiber), etc. can be used again. If filter shape is the above-mentioned ceramic sintered body and it is a honeycomb mutual weather-strip type, and textile fabrics and the nonwoven fabric of the above-mentioned ceramic fiber, it can mention what was wound around a certain substrate or was fabricated to desired

shape, for example. Although the above-mentioned monolith type filter in particular is not limited, using properly according to each characteristic is important for it. For example, although the filter which comprises a fiber is disadvantageous to raise collection efficiency, it is easy to be able to make pore-size distribution large comparatively and to apply it to exhaust air of broad PM particle diameter. Since especially the fiber is comparatively flexible, its contact probability with PM particles is high, and it is effective in processing of big PM particles which cannot react more easily. When carrying out division arrangement of the filter in two or more steps, it is good to allocate the filter which used the textile fabrics and/or the nonwoven fabric of ceramic fiber for the exhaust air upstream, and it good to allocate the honeycomb type filter which used the ceramic sintered body for the exhaust air downstream. Since a touch area can take a large honeycomb type filter also with small size comparatively, it is a typical filter of low-pressure-loss-quantity collection volume-quantity collection efficiency.

[0033]It is preferred for the filter with a catalyst function which made the above-mentioned monolith type filter support a catalyst component to divide into two or more steps and to arrange. In this case, since the filter with a catalyst function with which the exhaust air upstream and the downstream are different in the characteristic can be arranged, it is effective. For example, as shown in drawing 4, a filter with the above-mentioned catalyst function can be divided into two steps, and can be arranged in series. From this, the stoma passage distance of PM particles can be earned, and since the number of times of a collision of PM particles to the filter pore inside wall in which the catalyst component was supported increases, the efficiency of the above-mentioned HC generation reaction (formula 1) or the above-mentioned HC-NO reaction (formula 2) may improve substantially.

[0034]It is preferred to make pressure loss of the filter of the exhaust air upstream larger than the pressure loss of the filter of the exhaust air downstream in the filter with a catalyst function which carried out [above-mentioned] division arrangement. Usually, although division arrangement will raise pressure loss, that influence can be suppressed in this case. Also when this raises the contact probability of PM particles and a catalyst component, it is important, if it catches most PM particles with the filter of the upstream, becomes more superior [the rate of sedimentation] than reaction velocity, and tends to blockade a filter. The pressure loss of a filter can change and control porosity, an average pore diameter, etc. of a filter. As a result, PM collection efficiency can also be changed.

[0035]It is preferred to arrange a filter with comparatively low collection efficiency from the field of PM collection efficiency to the exhaust air upstream again, and to arrange a filter with high collection efficiency to the exhaust air downstream. In other words, it is good to make the average pore diameter and porosity of a filter of the exhaust air upstream larger than the average pore diameter and porosity of a filter of the exhaust air downstream. In this case, the effective use rate of C particles to HC generation is raised, and a NOx purification rate may improve.

[0036]Although PM particles of comparatively big particle diameter are caught by the filter of the exhaust air upstream at this time, whenever it contacts a catalyst component within a filter, a particle surface is changed into HC, and it moves in the inside of a stoma, reducing particle diameter. However, when there is a portion in which a catalyst component does not exist within a filter, it is fixed there and PM particles may serve as a core of a blockade. For this reason, its PM collection efficiency is low rather, the filter installed in the exhaust air upstream has an effective type which cannot cause a blockade easily, and it is preferred that it is a filter which has the so-called structure of a collision filtration method. For example, a form type, a fiber type, etc. which have three-dimensional meshes-of-a-net random structure are mentioned. Since PM particles by which, especially as for the above-mentioned fiber type filter, the part where the coat of the catalyst component was carried out was flexibly caught between fibers since it was able to expand and contract are movable, pushing away fiber particles by exhaust gas pressure. Since it is hard to blockade a filter stoma and the contact probability of a catalyst component and PM particles can be earned, a reaction is easy to be promoted. On the other hand, it is suitable for the exhaust air downstream to arrange the filter of high collection efficiency, high collection volume, and low pressure loss. It is because the characteristic which is the upstream

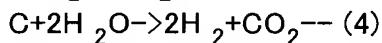
of catching certainly and making it reacting thoroughly since the grade reaction was carried out and low size is formed is required for PM particles of the exhaust air downstream. For example, the filter which has a surface filtration function can be used.

[0037]Although HC and SOF which are contained during exhaust air can raise purification efficiency by strengthening an adsorbing function and an oxidation function using a catalyst, If even a filter reaches, it may react to NOx on the catalyst component of a pore inside wall, or a pore inside wall, i.e., a catalyst surface, may be covered, and it may have an adverse effect, such as barring a catalysis. Then, the amount of [HC or] SOF is effective when promoting the alternative reaction of HC and NOx which carry out the trap upstream of the filter beforehand, and were generated from C within the filter demonstrates an exhaust-air-purification operation. It is preferred to specifically allocate in the exhaust air upstream of a filter the HC-SOF removal material which has the function to remove hydrocarbon and a soluble organic component. this -- 350 ** or less -- efficient purification of PM and NOx is comparatively attained also on low emission temperature conditions. HC-SOF removal material can be allocated, for example, as shown in drawing 3 or drawing 4. As a HC-SOF removal material, mordenite, MFI, beta type zeolite, and an average pore size can use conveniently the silica which is 1-5 nm or a laminar clay mineral and the zeolite concerning these arbitrary combination, and/or a silica content inorganic substance. As the above-mentioned silica, the porous body of the oxide called what is called mesoporous silica is mentioned, for example, it can obtain, using a surface-active agent as a mold. In less than 1 nm, the pole diameter of an average pore size is too small, when adsorption prehension with for [for HC / sufficient] cannot be performed but it exceeds 5 nm, a pole diameter is too large, and the adsorption efficiency for HC and SOF may fall. Hectorite, montmorillonite, etc. are mentioned as the above-mentioned laminar clay mineral. The oxidation removal of such porous body materials which used gaseous phase oxygen by adding catalyst components, such as Pt and Pd, while it is efficient and carrying out adsorption prehension of HC or the SOF by the upstream of a filter becomes possible, and the effective use rate of generation HC in a filter pore inside wall is raised. The above-mentioned porous body material can be coated and used for the honeycomb carrier made from what is called flow through type cordierite which has about 400 holes per square inch, for example. in order to coat a honeycomb body with the powder of this porous body and to make a honeycomb side pasted up and fixed -- alumina sol and silica -- it is common to use sintering agents (binder), such as sol. HC which stuck to porous body material, and the oxidation removal of SOF can be promoted by adding catalyst components, such as Pt and Pd. In this case, the powder which could make this porous body material support a catalyst component directly, and made carriers, such as alumina and a titania, support a catalyst component beforehand may be mixed and used for the charge powder of a porous material.

[0038]The exhaust emission control device mentioned above is obtained by making the above-mentioned noble metal component support with the impregnating method and/or plating, after making the pore inside wall of the above-mentioned monolith type filter carry out distributed support of the above-mentioned oxide particles. The impregnating method regularly used with the usual catalyst method of preparation is effective, and it is more effective to use plating which can cover a filter pore inside wall, and also using plating and the impregnating method together also has it. [effective] As plating, various kinds of methods are effective and can apply suitably an electrolytic decomposition process, a non-electrolytic decomposition process, etc. typically.

[0039]As mentioned above, in order not to use for the exhaust emission control device of this invention the exhaust air A/F variation control and also the NOx adsorbing function for removing the various exhaust air temperature-up control for burning PM deposited on the filter, and NOx, Specific control of S desorption control from a NOx adsorption catalyst, etc. is not needed, but aggravation of fuel consumption can be controlled. Since C can be purified at low temperature, there is no fear of breakage by the heat of a filter, and it can be equal to prolonged use. For example, in a diesel power plant, clean exhaust air can be realized and the cars excellent in economical efficiency (fuel consumption) with little environmental pollution including the problem of global warming can be provided.

[0040]Next, other exhaust-air-purification methods, exhaust purification catalysts, and exhaust emission control devices of this invention are explained in detail. This exhaust-air-purification method generates hydrogen from the soot (PM particles) adhering to a catalyst, and purifies NOx using the hydrogen. That is, when the temperature of the exhaust air discharged from an internal-combustion engine is 500 ** or less, they are the following reaction formula 3 and/or 4

$$\text{C} + \text{H}_2\text{O} \rightarrow \text{H}_2 + \text{CO} \quad \text{-- (3)}$$


It comes out and the hydrogen generating reaction expressed is performed. From this, hydrogen is generated from PM particles and even the temperature of 500 ** or less can purify NOx using this hydrogen.

[0041]Here, when using HC, CO, and also H₂ under exhaust air as a reducing agent of NOx, since a lot of oxygen exists, by lean atmosphere, these reducing agents will usually be H₂O and CO₂. Therefore, when lean atmosphere purified exhaust air of most operating conditions (lean burn engine etc.), there was fault that the above-mentioned hydrogen generating reaction (formulas 3 and 4) could not use effectively. In the lean atmosphere of hyperoxia, PM adhering to a catalyst hardly performs a steam and a hydrogen generating reaction (formulas 3 and 4).

[0042]PM which exists during exhaust air richly [the exhaust purification catalyst of this invention] regardless of Lean's atmosphere is made to adhere to a catalyst surface. And not only by a rich atmosphere but by lean atmosphere, this PM is mainly used for a hydrogen generating reaction (formulas 3 and 4) by operation of Rh, and hydrogen generates it. Therefore, NOx can be returned from the hydrogen generated also by lean atmosphere, and NOx purification performance can be improved. Since SOx of the NOx adsorption site by which sulfur poisoning was carried out can also be returned by hydrogen, while NOx adsorption capacity is recoverable, new sulfur poisoning can be prevented. NOx purification performance can be improved also by this.

[0043]Specifically as the above-mentioned H₂ generation catalyst, the thing containing the powder of the porosity particles which supported rhodium (Rh) at least, and iron (Fe), cobalt (Co), manganese (Mn) or nickel (nickel) and the metal concerning these arbitrary combination is used. At this time, metal, such as the above Fe, Co, Mn, and nickel, is good to be supported by the above-mentioned porosity particles. By using this H₂ generation catalyst, high NOx purification performance can be revealed by H₂ made to generate from PM and H₂O at the temperature of 500 ** or less. Since the reactivity of H₂ and NOx which were generated from PM and H₂O will improve in order to adsorb NOx by Lean if NOx adsorption material is used so that it may mention later and also the cleaning reaction of NOx can be promoted. When SOx under exhaust air reacts to a NOx adsorption site and forms SOx adsorption species and a SOx salt in a catalyst surface, NOx adsorption capacity may disappear (what is called sulfur poisoning), but since SOx is returned by the above-mentioned H₂ which made it generate, sulfur poisoning can be prevented. It is returned by H₂ and NOx adsorption capacity also tends to revitalize again the NOx adsorption site which received sulfur poisoning.

[0044]When metal, such as the above Fe, Co, Mn, and nickel, sets Rh to one, it is contained in the above-mentioned H₂ generation catalyst by the ratio of 0.1-10. It is more preferred that it is especially 1-5. If smaller than 0.1, the effect by these metal will not show up and it will not be different from the case of only Rh. On the other hand, if 10 is exceeded, the activity of Rh will fall, and the reactivity of PM and Rh will get worse. As for the above Rh, it is desirable to be supported in the per [porosity particle 120g / 0.05-20g] range. If there are few holding amounts of Rh than 0.05g/120g, endurance will fall easily, and if more than 20g/120g, while the above-mentioned effect will be saturated, it is easy to cause increase of cost. Platinum (Pt), palladium (Pd), iridium (Ir), etc. can also be supported with Rh, and the holding amount at this time should just make the sum total of Rh and these metal a mentioned range. As for Pt supported by the above-mentioned porosity particles, it is desirable that it is the range of per [porosity particle

120g / 0.1–10g]. If there are few holding amounts of Pt than 0.1g/120g, the purifying rate of HC, CO, and NOx will fall easily, and even if more than 10g/120g, while an effect is saturated, it is easy to cause increase of cost.

[0045]As the above-mentioned porosity particles, it can choose from alumina, silica, a titania, zirconia, silica alumina, zeolite, etc. suitably, and one sort can be used alone or two or more kinds can be used, for example, mixing or composite-izing. However, as for Zr with bad heat resistance, it is desirable to use alumina, zirconia, or zirconia alumina for Rh support powder from Reasons congenial to Rh. As for the particle diameter of the above-mentioned porosity particles, it is preferred that it is the range of 0.1–20 micrometers. If particle diameter is smaller than 0.1 micrometer, the degree of dispersion of Rh will fall, and the H₂ generation effect from PM and H₂O is fully hard to be acquired. If larger than 20 micrometers, the probability that Rh powder approaches will become high, the degree of dispersion of Rh falls as a result, and the H₂ generation effect by PM and H₂O may not fully be acquired.

[0046]The above-mentioned porosity particles can also be made to support NOx adsorption material further, and NOx adsorption capacity can be improved further in this case. As this NOx adsorbent, an alkaline metal, alkaline-earth metals or a rare earth metal, the metal concerning these arbitrary combination, etc. can be used. Specifically as an alkaline metal, lithium (Li), sodium (Na), potassium (K), caesium (Cs), etc. are mentioned. As alkaline-earth metals, magnesium (Mg), calcium (Ca), strontium (Sr), barium (Ba), etc. which are periodic table 2A group elements are mentioned. As a rare earth metal, a lanthanum (La), cerium (Ce), praseodymium (Pr), etc. are mentioned. As for this NOx adsorption material, it is desirable to make it support in 0.05–3.0 mol per 120g of porosity particles. If there are few holding amounts than 0.05 mol/120 g, even if a NOx purification rate will fall easily and it will support mostly from 3.0 mol/120 g, an effect is saturated easily. When the above-mentioned porosity particles are made to support Rh and Pt, in order to pull out enough an operation of metal, such as Rh, nickel and Fe, Co, and Mn, etc., it is good to manufacture independently Rh support porosity particles (the 1st powder) and Pt support porosity particles (the 2nd powder), and to mix these after that. In this case, the mixture ratio of the 1st powder and the 2nd powder has the desirable range of 1st powder:2nd powder =0.05:1–1:1 at weight ratio conversion of Rh and Pt. When both the 1st powder and the 2nd powder use alumina as porosity particles, the range of 1st powder:2nd powder =0.1:1–2:1 is desirable at weight ratio conversion of alumina. If it separates from these ranges, the case of the excess and deficiency of above-mentioned Rh and Pt and the same fault may occur. When the above-mentioned porosity particles are made to support a transition metal, it is desirable to make Mg support further. By using this co-catalyst, since a hydrogen generating reaction is easy to be promoted, it is effective.

[0047]In this invention, it can be considered as the exhaust emission control device which purifies the particulate particles and nitrogen oxides under exhaust air using an above-mentioned exhaust purification catalyst. That is, the exhaust emission control device of this invention allocates the above-mentioned hydrogen producing catalyst in the upstream of the engine smoke way of an internal-combustion engine, and allocates the above-mentioned nitrogen-oxides purifying catalyst in the downstream. By having such composition, it becomes an exhaust emission control device which promotes the above-mentioned hydrogen generating reaction (formulas 3 and 4). Other exhaust emission control devices of this invention allocate the layered product of the above-mentioned nitrogen-oxides purifying catalyst in engine smoke Michigami of an internal-combustion engine, and cover the above-mentioned hydrogen producing catalyst on it. For example, a NOx catalyst can be multilayered and Rh powder containing the metal which changes from Fe, Co, Mn or nickel, and these arbitrary combination to the top layer can be covered.

[0048]

[Example]Hereafter, although working example and a comparative example explain this invention still in detail, this invention is not limited to these working example.

[0049]In the following working example 1–3 and comparative examples 1–3, the performance

evaluation test was done about the exhaust emission control device of this invention, i.e., the exhaust emission control device which used the hydrocarbon (HC) generation catalyst.

[0050](Working example 1) To the nitric acid aqueous acids obtained by making the solution of an aluminium nitrate distribute super-particle alumina with a mean particle diameter of 0.5 micrometer. After dipping the product honeycomb type made from cordierite mutual weather-strip filter 2.5L which is 18 micrometers in 60% of porosity, and average pore diameter, and has a vent of about 200 cells per square inch, the hot-air-drying-baking process was repeated 3 times and the pore inside wall of the filter was made to carry out distributed support of the alumina. The holding amount of alumina at this time was about 85g per filter capacity 1L. This filter was dipped in the dinitrodiammine Pt solution whose Pt concentration is about 2.5%, the hot-air-drying-baking process was repeated twice, and the alumina made [the pore inside wall of the filter] to carry out distributed support was made to support Pt. Electroless deposition was performed to this filter and the filter catalyst 1A was acquired. Plating dipped the above-mentioned honeycomb filter in the plating bath solution containing Pt and a reducing agent, deposited Pt, and was obtained. The holding amount of Pt at this time was about 10g per filter capacity 1L.

[0051]The honeycomb shape monolith material (honeycomb catalyst 1B) which has a function which carries out adsorption treatment of HC and SOF which are arranged in the preceding paragraph of this filter catalyst 1A was obtained as follows. The Pt/gamma alumina powder which obtained it to it by the impregnating method by making the activated alumina which uses gamma alumina of specific surface area 2 [of about 220 m]/g as the main ingredients support Pt 2.5%, Specific surface area about 830m²/g and the porous silica of about 3.2 nm of average pore sizes, By specific surface area 2 [of 450 m]/g, the silica-alumina ratio about 90 zeolite beta. The MFI zeolite of the silica-alumina ratio 70 [about] was mixed by the weight ratio 1:4:1 by specific surface area 2 [of 350 m]/g, and it mixed by the weight ratio of 5:6:1 with boehmite powder, and also nitric acid acidity alumina sol was added 1%, it mixed with water, and slurry liquid was obtained. The cordierite honeycomb 1.5L which has a vent of 400 cells per square inch was coated with this slurry, and the honeycomb catalyst 1B which has a function which adsorbs and decomposes HC and SOF was acquired through the process of desiccation and calcination. The exhaust emission control device 1 was obtained by including in one converter in the preceding paragraph and the latter part, combining respectively the above, the honeycomb catalyst 1B, and the filter catalyst 1A.

[0052](Working example 2) A honeycomb catalyst was not installed in the preceding paragraph, but except having considered it only as the filter catalyst 2A, the same operation as working example 1 was repeated, and the exhaust emission control device 2 was obtained.

[0053](Working example 3) The product honeycomb type made from cordierite mutual weather-strip filter 1.25L which is 18 micrometers in 60% of porosity, and average pore diameter, and has a vent of about 200 cells per square inch, It was 32 micrometers in 65% of porosity, and average pore diameter, and the product honeycomb type made from cordierite mutual weather-strip filter 1.25L which has a vent of about 200 cells per square inch was prepared, the almost same operation as working example 1 was repeated, and two filter catalyst 3A₁ and 3A₂ were obtained. These filter catalyst 3A₁ and 3A₂, and the honeycomb catalyst 3B have been arranged in series, and the exhaust emission control device 3 was obtained. That is, these catalysts have been arranged from the exhaust air upstream in order of honeycomb catalyst 3B-filter catalyst 3A₂-filter catalyst 3A₁.

[0054](Comparative example 1) The Pt/gamma alumina powder which obtained it to it by the impregnating method by making the activated alumina which uses gamma alumina of specific surface area 2 [of about 220 m]/g as the main ingredients support Pt 2.5%, It mixed with boehmite powder by the weight ratio of 10:2, and also nitric acid acidity alumina sol was added 1%, it mixed with water, and slurry liquid was obtained. The cordierite honeycomb 1.5L which has a vent of 400 cells per square inch was coated with these 100 g/L of slurries, and the

honeycomb shape oxidation catalyst R1B was acquired through the process of desiccation and calcination. With this honeycomb shape oxidation catalyst R1B, and the porosity of 60% and the average pore diameter of 18 micrometers. The exhaust emission control device R1 which becomes the comparative example 1 was obtained by arranging in series the product honeycomb type made from cordierite mutual weather-strip filter 2.5L which has a vent of about 200 cells per square inch, and including in one converter. This device R1 has composition similar to what is called a conventional continuous reproduction type trap.

[0055](Comparative example 2) The same product honeycomb type made from cordierite mutual weather-strip filter 2.5L as working example 1 is coated with the slurry of the same Pt/gamma alumina catalyst as the comparative example 1. By repeating a hot-air-drying-baking process 4 times, one side of the filter was made to support Pt/alumina catalyst, and the filter catalyst R2A was acquired. The holding amount of Pt/alumina catalyst at this time was about 100g per filter capacity 1L. Only with this filter catalyst R2A, the exhaust emission control device R2 was obtained. This exhaust emission control device R2 does not make what changed the process of the filter catalyst, i.e., a filter wall surface, support Pt/alumina catalyst as compared with the exhaust emission control device 2 of working example 2, but forms a catalyst bed in a filter outer wall.

[0056](Comparative example 3) The exhaust emission control device R3 was obtained by arranging the honeycomb catalyst 1B same in the preceding paragraph of the same filter catalyst R2A as the comparative example 2 as working example 1, and including in one converter.

[0057]The performance evaluation test of the exhaust emission control device of working example and a comparative example was done using the engine dynamo device which installed the direct injection type diesel power plant of 4-cylinder 2.5L provided with the <example of evaluation test> common rail system. What can control the exhaust-gas temperature of a catalyst system entrance by post injection by engine load, an inhalation-of-air diaphragm, and a common rail system was used for this evaluation system. The transient-characteristics appraisal method which repeats the pattern which the quality assessment method of an exhaust emission control device holds the inlet temperature of a device at 250 ** for 2 minutes, and subsequently holds it at 300 ** for 3 minutes, and also is held for 1 minute at 350 ** for 5 hours was used. Sweden class 1 gas oil was used in this evaluation test.

[0058]In the above-mentioned evaluation test, when the average reduction rate of PM and NOx was computed about the exhaust emission control device 1 (working example 1), PM extraction ratio was 93% and the NOx extraction ratio was 46%. The pressure loss rise after 5-hour operation to the first stage was 25mmHg. Similarly, PM extraction ratio was [NOx of the reduction rate / in / about the exhaust emission control device 2 (working example 2) / operation 2 hours] 55% of an extraction ratio 90%. The pressure loss rise after 4-hour operation to the first stage is 32mmHg.

Covering of the catalyst component by SOF in PM takes place, and it seems that oxidation performance fell temporally.

By removing a part for SOF by the preceding paragraph side shows from this that prevent covering of a catalyst and endurance increases like the exhaust emission control device 1. About the exhaust emission control device 3 (working example 3), PM extraction ratio was 95% and the NOx extraction ratio was 57%. The pressure loss rise after 5-hour operation to the first stage was 18mmHg. This shows that the effect which divided the filter is demonstrated.

[0059]On the other hand, about the exhaust emission control device R1 (comparative example 1), PM extraction ratio was 95%, the NOx extraction ratio was 2%, and the NOx reduction rate was low compared with working example, and the pressure loss rise 3 hours after operation exceeded 40mmHg, and since the engine load became large, operation was canceled at the time. About the exhaust emission control device R2 (comparative example 2), PM extraction ratio is 92%, and a NOx extraction ratio is 8%, and the pressure loss rise 3 hours after [of operation] to the first stage exceeded 40mmHg, and since the engine load became large, operation was canceled at the time. About the exhaust emission control device R3 (comparative example 3), PM extraction ratio is 92%, and a NOx extraction ratio is 11%, and the pressure loss rise after 4-hour operation to the first stage exceeded 40mmHg, and since the engine load became large,

operation was canceled at the time.

[0060]Inlet temperature is held for the quality assessment conditions of an exhaust emission control device at 300 ** for 5 minutes, When it changes to the pattern held for 2 minutes at 400 more **, PM extraction ratio will be 91%, a NOx extraction ratio will be 16%, and, as for the average reduction rate of PM and NOx by the exhaust emission control device 1 after 5-hour operation, this shows that the reduction rate of NOx gets worse especially on high temperature exhaust gas conditions. An exhaust-gas temperature uses the exhaust emission control device of this invention on conditions 350 ** or less, since the effect is large, it is clear that it is suitable for the exhaust air purification of an efficient internal-combustion engine with a low exhaust-gas temperature, but. Correspondence will become possible if temperature conditions are adjusted by choosing a locating position suitably etc. also to an internal-combustion engine with a high exhaust-gas temperature.

[0061]As mentioned above, if the exhaust emission control device of this invention is used, about 200-350 ** since it is efficient and exhaust air of low emission temperature conditions can be purified comparatively, even if it does not use a special engine control method, clean exhaust air is easily realizable.

[0062]Next, in the following working example 4-9 and comparative examples 4-7, the performance evaluation test was done about the exhaust purification catalyst including the exhaust purification catalyst, i.e., the hydrogen (H_2) generation catalyst, and nitrogen-oxides (NOx) purifying catalyst of this invention.

[0063](Working example 4) Activated alumina powder (mean particle diameter of 1 micrometer) was impregnated, nitric acid Fe solution was calcinated at 400 ** among the after-desiccation air for 1 hour, and Fe support alumina powder (powder 1) was obtained. The Fe concentration of this powder was 2%. The powder 1 was impregnated, nitric acid Rh solution was calcinated at 400 ** after desiccation and among N_2 for 1 hour, and Rh and Fe support alumina powder (powder 2) were obtained. Rh concentration of this powder was 2% (Fe/Rh is a mole ratio and is 0.54). Activated alumina powder was impregnated, JIATORO diamine Pt solution was calcinated at 400 ** among the after-desiccation air for 1 hour, and Pt support alumina powder (powder 3) was obtained. Pt concentration of this powder was 2%.

[0064]70 g and alumina were thrown into 70 g, the water 140g was fed into the magnetic ball mill, preferential grinding of the powder 3 was carried out, and slurry liquid was obtained. After having adhered this slurry liquid to the nature monolith carrier of Caux Delight (1.3L, 400 cells), removing the slurry of the surplus in a cell in airstream and drying at 130 **, it calcinated at 400 ** for 1 hour, and coated layer weight the catalyst support of 140 g/L (A) was obtained. 70 g and the powder 3 were thrown into 70 g, the water 140g was fed into the magnetic ball mill, preferential grinding of the powder 2 was carried out, and slurry liquid was obtained. After having adhered this slurry liquid to catalyst support (A), removing the slurry of the surplus in a cell in airstream and drying at 130 **, it calcinated at 400 ** for 1 hour, and the total coated layer weight catalyst support of 280 g/L (B) was obtained. Catalyst support (B) was made to carry out catalyst 1L per 15g impregnating support of the acetic acid Ba solution by oxide conversion, and the exhaust purification catalyst (C) was acquired to it.

[0065](Working example 5) Except having used the nitric acid Co instead of the nitric acid Fe, the same operation as working example 1 was repeated, and the exhaust purification catalyst was acquired (CO/Rh is a mole ratio and is 0.57).

[0066](Working example 6) Except having used nitric acid nickel for the nitric acid Fe to be alike instead, the same operation as working example 1 was repeated, and the exhaust purification catalyst was acquired (nickel/Rh is a mole ratio and is 0.57).

[0067](Working example 7) Except having used nitric acid Mn instead of the nitric acid Fe, the same operation as working example 1 was repeated, and the exhaust purification catalyst was acquired (Mn/Rh is a mole ratio and is 0.53).

[0068](Working example 8) 140 g and alumina were thrown into 70 g, the water 280g was fed into the magnetic ball mill, preferential grinding of 70 g and the powder 3 was carried out for the almost same operation 2 as working example 1, i.e., powder, and slurry liquid was obtained. After

having adhered this slurry liquid to the nature monolith carrier of Caux Delight (1.3L, 400 cells), removing the slurry of the surplus in a cell in airstream and drying at 130 **, it calcinated at 400 ** for 1 hour, and coated layer weight the catalyst support of 280 g/L (B) was obtained. Catalyst support (B) was made to carry out catalyst 1L per 15g impregnating support of the acetic acid Ba solution by oxide conversion, and the exhaust purification catalyst (C) was acquired to it. [0069](Working example 9) Except having used zirconium oxide instead of activated alumina, the same operation as working example 1 was repeated, and the exhaust purification catalyst was acquired.

[0070](Comparative example 4) Activated alumina powder (mean particle diameter of 1 micrometer) was impregnated, nitric acid Rh solution was calcinated at 400 ** after desiccation and among N₂ for 1 hour, and Rh support alumina powder (powder 4) was obtained. Rh concentration of this powder was 2%. Activated alumina powder was impregnated, JIATORO diamine Pt solution was calcinated at 400 ** among the after-desiccation air for 1 hour, and Pt support alumina powder (powder 3) was obtained. Pt concentration of this powder was 2%. 70 g and alumina were thrown into 70 g, the water 140g was fed into the magnetic ball mill, preferential grinding of the powder 3 was carried out, and slurry liquid was obtained. After having adhered this slurry liquid to the nature monolith carrier of Caux Delight (1.3L, 400 cells), removing the slurry of the surplus in a cell in airstream and drying at 130 **, it calcinated at 400 ** for 1 hour, and coated layer weight the catalyst support of 140 g/L (A) was obtained. 70 g and the powder 3 were thrown into 70 g, the water 140g was fed into the magnetic ball mill, preferential grinding of the powder 2 was carried out, and slurry liquid was obtained. After having adhered this slurry liquid to catalyst support (A), removing the slurry of the surplus in a cell in airstream and drying at 130 **, it calcinated at 400 ** for 1 hour, and the total coated layer weight catalyst support of 280 g/L (B) was obtained. Catalyst support (B) was made to carry out catalyst 1L per 15g impregnating support of the acetic acid Ba solution by oxide conversion, and the exhaust purification catalyst (C) was acquired to it.

[0071](Comparative example 5) With the powder 1, except having made concentration of the nitric acid Fe 0.2%, the same operation as working example 1 was repeated, and the exhaust purification catalyst was acquired.

[0072](Comparative example 6) With the powder 1, except having made concentration of the nitric acid Fe 40%, the same operation as working example 1 was repeated, and the exhaust purification catalyst was acquired.

[0073](Comparative example 7) With the powder 1, except the mean particle diameter of the powder of activated alumina having been 50 micrometers, the same operation as working example 1 was repeated, and the exhaust purification catalyst was acquired.

[0074]The exhaust system of the engine with a [<the example of an evaluation test> and durable method displacement] of of 4400 cc was equipped with the exhaust purification catalyst, the catalyst inlet temperature of the preceding paragraph was 700 **, and it operated for 30 hours.

- The exhaust system of the engine of a valuation method diesel power plant was equipped with the exhaust purification catalyst, catalyst inlet temperature was 300 **, and it operated for 15 minutes. The exhaust purification catalyst was attached to the exhaust system of a gasoline engine, and it was considered as A/F=50 and the inlet temperature of 300 **, and operated for 10 minutes. It asked for the NOx inversion rate by the following formula NOx inversion rate =(1-catalyst outlet NOx quantity / catalyst inlet NOx quantity) x100%.

[0075]

[Table 1]

	貴金属		元素		M/Rh(モル比)	Rh担持多孔質体種	多孔質体の粒子系
	Pt g/L	Rh g/L	M g/L				
実施例4	2.8	1.4	Fe	1.4	0.54	Al ₂ O ₃	1 μm
実施例5	2.8	1.4	Co	1.4	0.57	Al ₂ O ₃	1 μm
実施例6	2.8	1.4	Ni	1.4	0.57	Al ₂ O ₃	1 μm
実施例7	2.8	1.4	Mn	1.4	0.53	Al ₂ O ₃	1 μm
実施例8	2.8	1.4	Fe	1.4	0.54	Al ₂ O ₃	1 μm
実施例9	2.8	1.4	Fe	1.4	0.54	ZrO ₂	1 μm
比較例4	2.8	1.4	なし	0	0.54	Al ₂ O ₃	1 μm
比較例5	2.8	1.4	Fe	0.14	0.054	Al ₂ O ₃	1 μm
比較例6	2.8	1.4	Fe	28.0	10.8	Al ₂ O ₃	1 μm
比較例7	2.8	1.4	Fe	1.4	0.54	Al ₂ O ₃	20 μm

[0076]

[Table 2]

	転化率%
	NOx
実施例4	82
実施例5	80
実施例6	80
実施例7	77
実施例8	79
実施例9	80
比較例4	50
比較例5	60
比較例6	68
比較例7	68

[0077]As shown in Table 1 and 2, the above-mentioned evaluation test shows that a NOx inversion rate is good in working example 4-9, even if it is comparatively low temperature exhaust air. On the other hand, in the comparative examples 4-7, it turns out that a NOx inversion rate is bad.

[0078]As mentioned above, although the preferred embodiment and the comparative example explained this invention in detail, this invention is not limited to these working example, and various modification is possible for it within the limits of the gist of this invention. For example, as for the catalyst of this invention, it is desirable to make an integral-construction type carrier support and to use. As an integral-construction type carrier, the monolith carrier which consists of heat-resistant material can use the carriers of products made from ceramics, such as Caux Delight, and metal, such as ferrite series stainless steel, desirably. The rate of exhaust air purification of NOx and PM can be raised by distinguishing a catalyst by different color with on a carrier.

[0079]

[Effect of the Invention]As explained above, according to this invention, it writes with once changing C particle (particulate particles) in PM into hydrocarbon or hydrogen, and raising the contact (collision) rate of a catalyst component and PM particles, and promoting this conversion reaction. The exhaust-air-purification method which can carry out self-consecration of NOx and the PM continuously without needing specific control under the usual burning conditions, an exhaust purification catalyst, and an exhaust emission control device can be provided.

[Translation done.]

(19)日本国特許庁 (J P)

(12) 公開特許公報 (A)

(11)特許出願公開番号
特開2002-361047
(P2002-361047A)

(43)公開日 平成14年12月17日 (2002.12.17)

(51)Int.Cl. ⁷	識別記号	F I	テ-マコ-ト ⁸ (参考)
B 0 1 D 53/94		B 0 1 D 39/14	B 3 G 0 9 0
39/14		39/20	D 3 G 0 9 1
39/20		B 0 1 J 23/42	A 4 D 0 1 9
53/86	Z A B	23/89	A 4 D 0 4 8
B 0 1 J 23/42		29/74	A 4 D 0 5 8

審査請求 未請求 請求項の数25 O.L (全 14 頁) 最終頁に統く

(21)出願番号	特願2001-167506(P2001-167506)	(71)出願人	000003997 日産自動車株式会社 神奈川県横浜市神奈川区宝町2番地
(22)出願日	平成13年6月1日 (2001.6.1)	(72)発明者	赤間 弘 神奈川県横浜市神奈川区宝町2番地 日産 自動車株式会社内
		(72)発明者	花木 保成 神奈川県横浜市神奈川区宝町2番地 日産 自動車株式会社内
		(74)代理人	100102141 弁理士 的場 基憲
			最終頁に統く

(54)【発明の名称】 排気浄化方法及び排気浄化装置

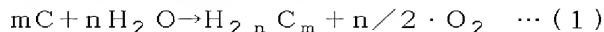
(57)【要約】

【課題】 通常の燃焼条件の下で、特定の制御を必要とせずにNO_xとPMを連続的に自己浄化することが可能な排気浄化方法、排気浄化触媒及び排気浄化装置を提供すること。

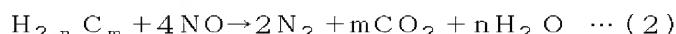
【解決手段】 $mC + nH_2O \rightarrow H_2, nC_m + n/2 \cdot O_2$ で表される反応によりPM粒子をHCに変換して排気中のPM粒子及びNO_xを浄化する方法である。モノリス型フィルタの気孔内壁に、貴金属と、平均粒径が1μm以下の酸化物微粒子と、を担持したフィルタを排気煙道に配設した排気浄化装置である。排気温度が500°C以下のときに、 $C + H_2O \rightarrow H_2 + CO$ 、 $C + 2H_2O \rightarrow 2H_2 + CO_2$ で表される水素生成反応を行い排気浄化する方法である。H₂生成触媒及びNO_x浄化触媒を含み、H₂生成触媒が、Rhを担持した多孔質粒子と、Fe、Co、Mn及びNiなどの金属とを含み、これら金属はRhを1としたときに0.1~10の比率で含まれる排気浄化触媒である。

【特許請求の範囲】

【請求項1】 排気中のパーティキュレート粒子及び窒



で表される反応によりパーティキュレート粒子を炭化水素に変換する過程を含むことを特徴とする排気浄化方法。



で表される反応により窒素、二酸化炭素及び水に変換する過程を含むことを特徴とする請求項1に記載の排気浄化方法。

【請求項3】 上記反応式1で表される反応を、350°C以下の温度で行うことを特徴とする請求項1又は2に記載の排気浄化方法。

【請求項4】 上記反応式1で表される反応を、280°C以下の温度で行うことを特徴とする請求項3に記載の排気浄化方法。

【請求項5】 上記反応式2で表される反応を、350°C以下の温度で行うことを特徴とする請求項1~4のいずれか1つの項に記載の排気浄化方法。

【請求項6】 上記反応式2で表される反応を、280°C以下の温度で行うことを特徴とする請求項5に記載の排気浄化方法。

【請求項7】 請求項1~6のいずれか1つの項に記載の排気浄化方法を用いて排気中のパーティキュレート粒子及び窒素酸化物を浄化する装置であって、モノリス型フィルタの気孔内壁に、白金、パラジウム及びロジウムから成る群より選ばれた少なくとも1種の貴金属成分と、平均粒径が1μm以下であるアルミナ、チタニア、ジルコニア及びシリカから成る群より選ばれた少なくとも1種の酸化物微粒子と、を担持して成る触媒機能付きフィルタを内燃機関の排気煙道に配設したことを特徴とする排気浄化装置。

【請求項8】 上記酸化物微粒子の平均粒径が0.6μm以下であることを特徴とする請求項7に記載の排気浄化装置。

【請求項9】 上記モノリス型フィルタの気孔率が30~80%であり、平均気孔径が5~40μmであることを特徴とする請求項7又は8に記載の排気浄化装置。

【請求項10】 上記触媒機能付きフィルタが、2段以上に分割され直列に配置されて成ることを特徴とする請求項7~9のいずれか1つの項に記載の排気浄化装置。

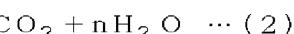
【請求項11】 排気上流側の触媒機能付きフィルタの圧力損失が、排気下流側の触媒機能付きフィルタの圧力損失より大きいことを特徴とする請求項10に記載の排気浄化装置。

【請求項12】 排気上流側の触媒機能付きフィルタの平均気孔径が、排気下流側の触媒機能付きフィルタの平均気孔径より大きいことを特徴とする請求項10又は11に記載の排気浄化装置。

【請求項13】 排気上流側の触媒機能付きフィルタの

素酸化物を浄化する方法であって、次の反応式1

【請求項2】 上記炭化水素を窒素酸化物と反応させ、次の反応式2



気孔率が、排気下流側の触媒機能付きフィルタの気孔率より大きいことを特徴とする請求項10~12のいずれか1つの項に記載の排気浄化装置。

【請求項14】 上記排気上流側の触媒機能付きフィルタが、衝突渦過機能を有することを特徴とする請求項10~13のいずれか1つの項に記載の排気浄化装置。

【請求項15】 上記排気下流側の触媒機能付きフィルタが、表面渦過機能を有することを特徴とする請求項10~14のいずれか1つの項に記載の排気浄化装置。

【請求項16】 上記排気上流側の触媒機能付きフィルタが、セラミック繊維の織布及び/又は不織布を用いて成ることを特徴とする請求項10~15のいずれか1つの項に記載の排気浄化装置。

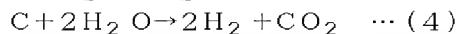
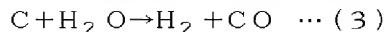
【請求項17】 上記排気下流側の触媒機能付きフィルタが、セラミック焼結体を用いて成ることを特徴とする請求項10~16のいずれか1つの項に記載の排気浄化装置。

【請求項18】 上記触媒機能付きフィルタの排気上流側に、炭化水素及び可溶性有機成分を除去する機能を有するHC・SOF除去材料を配設して成ることを特徴とする請求項10~17のいずれか1つの項に記載の排気浄化装置。

【請求項19】 上記HC・SOF除去材料が、モルデナイト、MFI、β型ゼオライト、平均細孔径が1~5nmであるシリカ、及び層状粘土鉱物から成る群より選ばれた少なくとも1種のゼオライト及び/又はシリカ含有無機物であることを特徴とする請求項18に記載の排気浄化装置。

【請求項20】 請求項7~19のいずれか1つの項に記載の排気浄化装置を製造する方法であって、上記モノリス型フィルタの気孔内壁に上記酸化物微粒子を分散担持させた後に、上記貴金属成分を含浸法及び/又はメッキ法によって担持させることを特徴とする排気浄化装置の製造方法。

【請求項21】 排気中のパーティキュレート粒子及び窒素酸化物を浄化する方法であって、内燃機関から排出される排気の温度が500°C以下のとき、次の反応式3及び/又は4



で表される水素生成反応を行う過程を含むことを特徴とする排気浄化方法。

【請求項22】 請求項21に記載の排気浄化方法に用

いられる水素生成触媒及び窒素酸化物浄化触媒を含む排気浄化触媒であって、

上記水素生成触媒が、少なくともロジウムを担持した多孔質粒子の粉末と、鉄、コバルト、マンガン及びニッケルから成る群より選ばれた少なくとも1種の金属とを含み、これら金属はロジウムを1としたときに0.1~1.0の比率で含まれることを特徴とする排気浄化触媒。

【請求項23】 上記多孔質粒子の平均粒子径が、0.1~2.0μmであることを特徴とする請求項22に記載の排気浄化触媒。

【請求項24】 請求項22又は23に記載の排気浄化触媒を用いて排気中のパーティキュレート粒子及び窒素酸化物を浄化する装置であって、内燃機関の排気煙道の上流側に上記水素生成触媒を配設し、その下流側に上記窒素酸化物浄化触媒を配設して成ることを特徴とする排気浄化装置。

【請求項25】 請求項22又は23に記載の排気浄化触媒を用いて排気中のパーティキュレート粒子及び窒素酸化物を浄化する装置であって、内燃機関の排気煙道上に上記窒素酸化物浄化触媒の積層体を配設し、その上に上記水素生成触媒を被覆して成ることを特徴とする排気浄化装置。

【発明の詳細な説明】

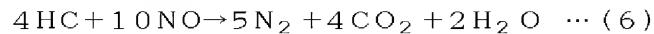
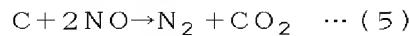
【0001】

【発明の属する技術分野】本発明は、排気浄化方法、排気浄化触媒及び排気浄化装置に係り、更に詳細には、内燃機関などから発生する排気中のパーティキュレート(PM)粒子と窒素酸化物(NO_x)を高効率で浄化し得る排気浄化方法、排気浄化触媒及び排気浄化装置に関する。

【0002】

【従来の技術及び発明が解決しようとする課題】近年、燃費向上及び二酸化炭素排出量の削減の観点から、理論空燃比より高い空燃比でも運転するリーンバーンエンジンが普及してきている。特に、ディーゼルエンジンは、その低燃費のゆえに改めて注目されている。

【0003】しかしながら、排気中に固体粒子分であるPMを含み、且つ排気温度が低いことから、従来型の触媒では高効率の排気浄化が困難な状況にある。昨今はエンジンの燃費向上技術が格段に進歩し、排気温度が更に低下する傾向にあるために、排気の浄化は、ますます困難となってきており、ディーゼルエンジンの排気中の有害成分を高効率浄化できる有効な方法が望まれている。従来のディーゼルエンジンの排気浄化用触媒としては、白金(Pt)をアルミナ(Al₂O₃)等の耐火性高表面積無機担体材料に担持してなる酸化触媒が用いられているが、COとHCの酸化が主機能であり、SO₂分もある程度は酸化できるものの、PMの主成分であるドラ



イスト(C=炭素粒子)の浄化には効力を示さない。

【0004】ディーゼルエンジンの排気のようにPM分を含有する排気を浄化するには、フィルタ技術が不可欠であり、コーチュライトや炭化珪素から成る多孔質焼結体や纖維状のフィルタが多数提案されている。なお、上記纖維状フィルタの素材としては、アルミナやシリカ等各種材料からなるものも提案されている。また、自動車技術会 学術講演会前刷集 No. 103-98(1998年秋季大会)には、炭化珪素纖維を用いたディーゼル・パーティキュレート・フィルタ(DPF)が提案されているが、トラップしたPMを除去してフィルタを再生するためのヒーターが不可欠であり、複雑なシステムが必要であることから、搭載スペースが少ない乗用車には適用が困難である。

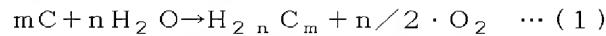
【0005】また、ヒーターを用いないでフィルタを再生する方法として、フィルタの前段にPt系触媒を配置させることによって排気中のNOを酸化力の強いNO₂に転化し、このNO₂の酸化力をを利用してフィルタにトラップしたPM分を燃焼する方法が提案されている(特開平1-318715号公報, J. P. Warren, et. al., "Effects on after-treatment on particulate matter when using the Continuously Regenerating Trap", I mechE 1998 S491/006, B. Carberry, et. al., "A focus on current and future particle after-treatment systems", I mechE 1998 S491/007)。この方法は、排気中の成分同士の反応を利用したもので、トラップしたPM分を連続的に燃焼浄化できることから、連続再生式トラップと呼ばれている。しかし、PM中のカーボン(C)は固体粒子であるために、NO₂との反応速度は比較的遅く、エンジンから排出されたCを十分な速度で燃焼させるためには、排気の条件が400°C以上の比較的高い温度条件を要すること、更には、そのような温度域で酸化剤となるNO₂量を増加することが必要となる。即ち、エンジンからのNO_x排出量を増やすことが必要になり、その結果、増えたNO_xを浄化するために高性能のNO_x触媒が必要となる。

【0006】PMとNO_xを同時に浄化するための各種方法も提案されている。例えば、特開平7-116519号公報には、多孔質フィルタにペロブスカイト構造を有する触媒を担持してなる排ガス浄化材が提案されており、これは排ガス中に含まれる微粒子状物質及び/又は炭化水素を還元剤として作用させ、排気中の窒素酸化物を還元する方法であり、該触媒を用い下記反応式5及び6

で表される反応によりNO_xを還元するとされている。上記反応において、反応式6は気体分子同士の反応であることから触媒作用が期待されるのに対し、反応式5は固体と気体との反応であるため触媒作用を期待することは難しく、通常の走行モード条件下でフィルタ再生ができるかは不明である。

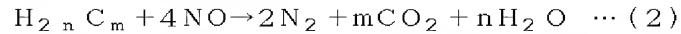
【0007】一方、特許掲載第2722987号公報には、NO_x吸収剤とフィルタを伝熱可能な位置に配置してNO_x吸収剤からNO_x放出還元後にPMを燃焼させることが提案されている。また、特開平9-94434号公報には、NO_x吸収剤をウォールフロー型フィルタの隔壁気孔内部に担持して、フィルタとNO_x吸収剤を一体化した触媒が提案されている。

【0008】これらはNO_xを処理する触媒とフィルタとを組み合わせて得られる技術であり、NO_x処理とPM燃焼のためにそれぞれ別のエンジン制御を必要とする。NO_x吸収剤を働かせてNO_xを吸収、還元するためには排気の空燃比(A/F)を変える制御が必要である。また、フィルタを再生させるための堆積PMの燃焼、及びNO_x吸収剤にトラップされた硫黄化合物の除去には、NO_x吸収剤及び/又はフィルタを600°Cあるいはそれ以上にまで昇温させる必要があり、更にNO_x吸収剤からの硫黄化合物の除去は還元雰囲気下で行うのに対し、フィルタの再生は酸化雰囲気条件で行うことが必要である。更にまた、高温化により触媒の劣化を促進し、システム的にも高コスト化するという問題点がある。



で表される反応によりパーティキュレート粒子を炭化水素に変換する過程を含むことを特徴とする。

【0012】また、本発明の排気浄化方法の好適形態



で表される反応により窒素、二酸化炭素及び水に変換する過程を含むことを特徴とする。

【0013】更に、本発明の排気浄化装置は、上記排気浄化方法を用いて排気中のパーティキュレート粒子及び窒素酸化物を浄化する装置であって、モノリス型フィルタの気孔内壁に、白金、パラジウム及びロジウムから成る群より選ばれた少なくとも1種の貴金属成分と、平均粒径が1μm以下であるアルミナ、チタニア、ジルコニア及びシリカから成る群より選ばれた少なくとも1種の酸化物微粒子と、を担持して成る触媒機能付きフィルタを内燃機関の排気煙道に配設したことを特徴とする。

【0014】更にまた、本発明の排気浄化装置の好適形態は、上記モノリス型フィルタの気孔率が30~80%であり、平均気孔径が5~40μmであることを特徴とする。

【0015】また、本発明の排気浄化装置の他の好適形態は、上記触媒機能付きフィルタが、2段以上に分割され直列に配置されて成ることを特徴とする。

【0016】更に、本発明の排気浄化装置の更に他の好

る。このような排気温度や雰囲気(A/F)の制御は複雑であり、また、燃費や運転性の犠牲を伴うことから、通常の走行条件の下で特定の制御を加えることなく連続的に自己浄化可能な排気浄化方法が切望されている。また、PM、NO_xの同時除去を目的に、フィルタに触媒を担持する提案がなされているが、触媒成分とPM粒子との接触あるいは衝突確率という観点からの工夫はなれていた。

【0009】本発明は、このような従来技術にの有する課題に鑑みてなされたものであり、その目的とするところは、通常の燃焼条件の下で、特定の制御を必要とせずにNO_xとPMを連続的に自己浄化することが可能な排気浄化方法、排気浄化触媒及び排気浄化装置を提供することにある。

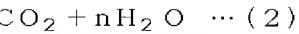
【0010】

【課題を解決するための手段】本発明者らは、上記課題を解決すべく鋭意検討を重ねた結果、PM中のC固体粒子(パーティキュレート粒子)を一旦炭化水素や水素に変換すること、触媒成分とPM粒子との接触(衝突)率を高めて該変換反応を促進させることにより、上記課題が解決できることを見出し、本発明を完成するに至った。

【0011】即ち、本発明の排気浄化方法は、排気中のパーティキュレート粒子及び窒素酸化物を浄化する方法であって、次の反応式1



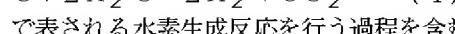
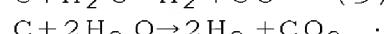
は、上記炭化水素を窒素酸化物と反応させ、次の反応式2



適形態は、上記触媒機能付きフィルタの排気上流側に、炭化水素及び可溶性有機成分を除去する機能を有するHC・SOF除去材料を配設して成ることを特徴とする。

【0017】更にまた、本発明の排気浄化装置の製造方法は、上記排気浄化装置を製造する方法であって、上記モノリス型フィルタの気孔内壁に上記酸化物微粒子を分散担持させた後に、上記貴金属成分を含浸法及び/又はメッキ法によって担持させることを特徴とする。

【0018】また、本発明の他の排気浄化方法は、排気中のパーティキュレート粒子及び窒素酸化物を浄化する方法であって、内燃機関から排出される排気の温度が500°C以下のときに、次の反応式3及び/又は4



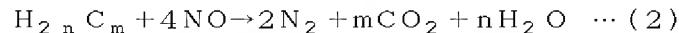
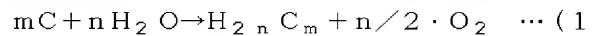
で表される水素生成反応を行う過程を含むことを特徴とする。

【0019】更に、本発明の排気浄化触媒は、上記排気浄化方法に用いられる水素生成触媒及び窒素酸化物浄化触媒を含む排気浄化触媒であって、上記水素生成触媒

が、少なくともロジウムを担持した多孔質粒子の粉末と、鉄、コバルト、マンガン及びニッケルから成る群より選ばれた少なくとも1種の金属とを含み、これら金属はロジウムを1としたときに0.1～10の比率で含まれることを特徴とする。

【0020】更にまた、本発明の他の排気浄化装置は、上記排気浄化触媒を用いて排気中のパーティキュレート粒子及び窒素酸化物を浄化する装置であって、内燃機関の排気煙道の上流側に上記水素生成触媒を配設し、その下流側に上記窒素酸化物浄化触媒を配設して成ることを特徴とする。

【0021】また、本発明の更に他の排気浄化装置は、上記排気浄化触媒を用いて排気中のパーティキュレート粒子及び窒素酸化物を浄化する装置であって、内燃機関の排気煙道上に上記窒素酸化物浄化触媒の積層体を配設し、その上に上記水素生成触媒を被覆して成ることを特徴とする。



で表される変換反応を進行させることでNO_x及びPMがほぼ同時に除去される。ここで、CとH₂OによるHC生成反応(式1)において、PM中のCがHCに変換されるメカニズムの詳細は現時点では不明であるが、本発明者らは、例えば、Pt/アルミナ系触媒を、C(グラファイト)/O₂/H₂O/N₂系のモデルガスと反応させた評価を行い、図1のグラフに示すように、HCを検出した。また、モデルガス中にNOを追加導入して評価を行い、図2に示すように、NO濃度が減少することを確認した。従って、HC生成反応(式1)及びHC-NO反応(式2)が起こっていることが推察できる。

【0025】更に、上記HC生成反応(式1)及びHC-NO反応(式2)を進行させるには、一例である図1及び図2のグラフからもわかるように、温度条件を350℃以下とすることが好ましく、特に280℃以下とすることがより好ましい。なお、下限温度は、触媒の性能などにより異なるが、概ね200℃以上の温度であれば顕著な反応速度が得られる。ここで、350℃より高い温度条件では、上記HC生成反応(式1)で生成したHCの酸化反応が優勢となり、上記HC-NO反応(式2)も劣勢となると考えられる。一方、酸素の多い排気条件(リーンバーンエンジンなど)におけるPt系触媒上でのHC-NO_x反応(式2)は、概ね150℃～300℃の温度域で顕著に進行することが知られている。このように、本発明の排気浄化方法を用いれば、上記HC生成反応(式1)及びHC-NO反応(式2)を比較的低温条件で進行させ得るので、PMが重大な問題となっているディーゼルエンジンからの排気を特定のエンジン制御を行わずに高効率で浄化できる。

【0026】次に、本発明の排気浄化装置について詳細に説明する。上述のHC生成反応(式1)や上記HC-NO反応(式2)を進行させるには、触媒を使用するこ

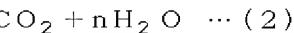
とを特徴とする。

【0022】

【発明の実施の形態】以下、本発明の排気浄化方法について詳細に説明する。なお、本明細書において「%」は特記しない限り、質量百分率を示す。

【0023】本発明の排気浄化方法は、排気中のパーティキュレート(PM)粒子及び窒素酸化物(NO_x)を浄化する方法であって、PM粒子を炭化水素(HC)に変換することにより、通常の走行条件では燃焼し難い排気中のPM粒子を高効率で浄化することを特徴とする。また、生成したHCを排気中のNO_xと反応させることで、NO_xは無害な窒素(N₂)、CO₂及びH₂Oに変換される。なお、生成したHCは、直ちに酸化して二酸化炭素(CO₂)や水(H₂O)に変換しても良い。

【0024】即ち、本発明の排気浄化方法では、次の反応式1及び2



とが必須条件であるが、本発明者らは、かかる反応では触媒とPM粒子とが直接接触することが大変有効であることを知見した。例えば、上記HC生成反応(式1)は、Pt/アルミナ系触媒粉末とカーボン(C)粉末とを十分に良く混合した場合にのみ進行し、混合が不十分な場合には進行しない。本発明の排気浄化装置は、かかる観点から触媒成分とPM粒子との接触(衝突)確率を高める手段として、渦過機能を積極的に利用する。即ち、渦過機能及び触媒機能を有する排気浄化装置とし、フィルタの気孔内壁表面上に触媒成分を分散、担持させることで、狭い気孔内に流入してくるPM粒子と触媒成分との接触(衝突)確率を高める。なお、上記触媒成分の担持方法としては、後述するように、メッキ法などにより内壁一面を被覆する担持方法が有効である。

【0027】ここで、本発明の排気浄化装置は、具体的には、モノリス型フィルタの気孔内壁に、上記触媒成分として、白金(Pt)、パラジウム(Pd)又は(Rh)、及びこれらの任意の組合せより成る貴金属成分を担持させて成る。このとき、貴金属成分は、特に単独で使用する必要はなく、2成分以上を組合せて使用するときは、上記HC生成反応(式1)及びHC-NO反応(式2)をより円滑に進めることができる。例えば、PtとRhの組合せでは、PtでHC生成反応(式1)を促進させ、RhでHC-NO反応(式2)を促進させることができる。

【0028】また、上記モノリス型フィルタの気孔内壁には、平均粒径が1μm以下の微粉の酸化物粒子、具体的には、貴金属成分の担体として従来から用いられているアルミナ(Al₂O₃)、チタニア(TiO₂)、ジルコニア(ZrO₂)又はシリカ(SiO₂)、及びこれらの任意の組合せに係る酸化物微粒子を担持させる。これより、気孔が閉塞されず、気孔内壁の表面に触媒成

分が良好に分散する。更に、上記平均粒径は0.6 μm 以下であることがより好ましい。更にまた、上記酸化物微粒子は、単独でも使用できるが、2種以上の触媒成分を担持するときなどは2種以上の酸化物微粒子を組合せて使用するとより効果的なことがある。なお、平均粒径が1 μm を超えると上記モノリス型フィルタの気孔が閉塞されてしまうことがある。また、上記酸化物微粒子は、該酸化物微粒子を生成し得る水酸化物や硝酸塩の水溶液をフィルタの気孔内壁に浸透させ、分散担持させることができる。

【0029】更に、上記貴金属成分や酸化物微粒子の担持方法としては、酸化物微粒子の粉末をフィルタ気孔内壁に浸透担持させ、次いで貴金属成分を担持させる方法や、貴金属成分を予め酸化物微粒子に担持させた後、該酸化物微粒子をフィルタ気孔内壁に浸漬担持させる方法などが例示できる。特に、貴金属成分をできるだけ粒子表面側に露出させると、前者がより有効である。

【0030】更にまた、上記貴金属成分や酸化物微粒子の担体としては、渦過機能を有するモノリス型のフィルタを使用する。このとき、該モノリス型フィルタは、フィルタとしての基本特性が優れていること、即ち、高捕集率・高捕集量・低圧損であることが望ましい。また、触媒成分（貴金属成分）を気孔内壁表面に担持でき、この触媒成分を排気中のPM粒子と高い確率で接触させ得ることがよい。

【0031】また、上記モノリス型フィルタにおいて、気孔率は30～80%であることが好適である。気孔率が30%未満であると、所定の性能を満たすためのフィルタサイズを大きくとらなくてはならず、搭載性が悪化することがある。また、80%を超えると強度が低下し、搭載性が悪化することがある。更に、気孔径は平均気孔径で5～40 μm であることが好適である。このときは、気孔の大きさが担持する触媒成分の粒径に適切であり、PM粒子が容易に侵入可能となり気孔壁との接触確率を増大できるので有効である。5 μm より小さいとPM粒子の侵入が困難となり、侵入しても気孔内を移動し難いことがある。一方、40 μm より大きいとPM粒子と気孔壁との接触確率が低下し、反応せずに気孔内を通過してしまうことになる。

【0032】更にまた、上記モノリス型フィルタとしては、コーボライト、ムライト及びSiC等のセラミック焼結体や、セラミック繊維（ファイバ）の繊布及び／又は不繊布などを用いることができる。また、フィルタ形状は、例えば、上記セラミック焼結体であればハニカム交互目詰めタイプ、上記セラミック繊維の繊布や不繊布であれば何らかの基材に巻いたり所望形状に成形したものなどを挙げることができる。なお、上記モノリス型フィルタは、特に限定されないが、それぞれの特性に合わせて使い分けることが重要である。例えば、ファイバから成るフィルタは、捕集効率を高めるには不利である

が、気孔径分布を比較的広くすることが可能であり、幅広いPM粒子径の排気に適用し易い。特に、ファイバは比較的フレキシブルであるためPM粒子との接触確率が高く、より反応し難い大きなPM粒子の処理に有効である。また、フィルタを2段以上に分割配置する場合は、排気上流側にセラミック繊維の繊布及び／又は不繊布を用いたフィルタを配設することがよく、排気下流側にセラミック焼結体を用いたハニカム型フィルタを配設することがよい。なお、ハニカム型フィルタは、比較的小なサイズでも接触面積が大きく取れるため、低圧損・高捕集量・高捕集率の代表的なフィルタである。

【0033】また、上記モノリス型フィルタに触媒成分を担持させた触媒機能付フィルタは、2段以上に分割して配置することが好適である。この場合は、排気上流側と下流側とで特性の違った触媒機能付フィルタを配置できるので有効である。例えば、図4に示すように、上記触媒機能付フィルタを2段に分割し直列に配置することができる。これより、PM粒子の気孔通過距離を稼ぐことができ、触媒成分が担持されたフィルタ気孔内壁へのPM粒子の衝突回数が増大するため、上記HC生成反応（式1）や上記HC-NO反応（式2）の効率が大幅に向上し得る。

【0034】更に、上記分割配置した触媒機能付フィルタでは、排気上流側のフィルタの圧力損失を排気下流側のフィルタの圧力損失より大きくすることが好適である。通常、分割配置は圧力損失を高めてしまうが、この場合は、その影響を抑えることができる。これはPM粒子と触媒成分との接触確率を高める上でも重要であり、上流側のフィルタでPM粒子の大部分を捕捉すると、反応速度よりも堆積速度が優勢となり、フィルタが閉塞し易い。なお、フィルタの圧力損失は、フィルタの気孔率や平均気孔径などを変更して制御できる。その結果、PM捕集率も変更できる。

【0035】更にまた、PM捕集率の面から、排気上流側には比較的捕集率の低いフィルタを配置し、排気下流側には捕集率の高いフィルタを配置することが好ましい。言い換れば、排気上流側のフィルタの平均気孔径や気孔率を、排気下流側のフィルタの平均気孔径や気孔率より大きくすることがよい。この場合は、HC生成に対するC粒子の有効利用率が高められ、NOx浄化率が向上し得る。

【0036】このとき、排気上流側のフィルタには、比較的大な粒径のPM粒子が捕捉されるが、フィルタ内で触媒成分と接触する度に粒子表面がHCに変換され、粒径を減らしながら気孔内を移動する。しかし、フィルタ内で触媒成分が存在しない部分があると、PM粒子はそこに固定され閉塞の核となってしまうことがある。このため、排気上流側に設置するフィルタは、PM捕集率がむしろ低く、閉塞を起こし難いタイプが有効であり、いわゆる衝突渦過方式の構造を有するフィルタであるこ

とが好ましい。例えば、3次元網目ランダム構造を有するフォーム型、ファイバ型などが挙げられる。特に、上記ファイバ型のフィルタは、触媒成分がコートされた部位がフレキシブルに伸縮可能であるため、ファイバ間に捕捉されたPM粒子は排気圧力によってファイバ粒子を押しのけながら移動できるので、フィルタ気孔が閉塞し難く、また、触媒成分とPM粒子との接触確率が稼げるため、反応が促進され易い。一方、排気下流側には、高捕集率、高捕集量及び低圧損のフィルタを配置することが好適である。排気下流側のPM粒子は、上流側である程度反応して低サイズ化しているので、確実に捉えて完全に反応させる特性が必要だからである。例えば、表面渦過機能を有するフィルタを用いることができる。

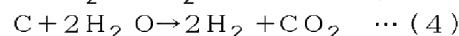
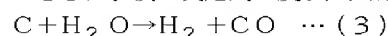
【0037】また、排氣中に含まれているHCやSOFは、触媒を用いて吸着機能と酸化機能を強化することにより、浄化効率を高めることができるが、フィルタまで到達すると気孔内壁の触媒成分上でNO_xと反応したり、気孔内壁、即ち触媒表面を覆ったりして、触媒作用を妨げるなどの悪影響を及ぼす可能性がある。そこで、HCやSOF分は、予めフィルタの上流でトラップしておき、フィルタ内でCから生成したHCとNO_xとの選択性的反応を促進することが排気浄化作用を発揮する上で有効である。具体的には、フィルタの排気上流側に、炭化水素及び可溶性有機成分を除去する機能を有するHC・SOF除去材料を配設することができる。これより、350°C以下の比較的低排温条件でもPMとNO_xの高効率浄化が可能になる。HC・SOF除去材料は、例えば、図3又は図4に示すように配設できる。また、HC・SOF除去材料としては、モルデナイト、MFI、 β 型ゼオライト、平均細孔径が1~5nmであるシリカ又は層状粘土鉱物、及びこれらの任意の組合せに係るゼオライト及び/又はシリカ含有無機物を好適に使用できる。なお、上記シリカとしては、いわゆるメソポーラスシリカと称せられる酸化物の多孔体が挙げられ、例えば、界面活性剤を錆型として用いて得ることができる。平均細孔径が1nm未満では細孔径が小さすぎてHC、SOF分の十分な吸着捕捉ができず、5nmを超えると細孔径が大きすぎてHC、SOF分の吸着効率が低下することがある。また、上記層状粘土鉱物としては、ヘクトライト、モンモリロナイト等が挙げられる。これらの多孔体材料は、フィルタの上流側でHCやSOFを高効率で吸着捕捉するとともに、更にPtやPd等の触媒成分を添加することにより、気相酸素を利用した酸化除去が可能となり、フィルタ気孔内壁における生成HCの有効利用率が高められる。上記多孔体材料は、例えば、1平方インチ当たり400個程度の孔を有する、いわゆるフロースルー型のコージェライト製のハニカム担体にコーティングして用いることができる。該多孔体の粉末をハニカム体にコーティングしてハニカム面に接着・固定させるためには、アルミナゾル、シリカゾルなど

の焼結剤（バインダー）を用いるのが一般的である。また、PtやPd等の触媒成分を添加することにより、多孔体材料に吸着したHCやSOFの酸化除去を促進することができる。この場合、該多孔体材料に直接触媒成分を担持させても良いし、アルミナやチタニア等の担体に触媒成分を予め担持させた粉末を多孔材料粉に混合して用いても良い。

【0038】上述した排気浄化装置は、上記モノリス型フィルタの気孔内壁に上記酸化物微粒子を分散担持させた後に、上記貴金属成分を含浸法及び/又はメッキ法によって担持させて得られる。なお、通常の触媒調製法で常用される含浸法も有効であるが、フィルタ気孔内壁を被覆できるメッキ法を用いるのがより効果的であり、更にメッキ法と含浸法とを併用することも有効である。メッキ法としては、各種の方法が有効であり、代表的には電解法や無電解法などを適宜適用できる。

【0039】以上のように、本発明の排気浄化装置は、フィルタに堆積したPMを燃焼させるための各種排気昇温制御、NO_xを除去するための排気A/F変動制御、更にはNO_x吸着機能を使わないと、NO_x吸着触媒からのS脱離制御等の特定の制御を必要とせず、燃費の悪化を抑制できる。また、低温でCを浄化できるため、フィルタの熱による破損の恐れがなく、長期間の使用に耐えられる。例えば、ディーゼルエンジンにおいて、クリーンな排気を実現することができ、地球温暖化の問題を含めて環境汚染が少ない、経済性（燃費）に優れた自動車を提供することができる。

【0040】次に、本発明の他の排気浄化方法、排気浄化触媒及び排気浄化装置について詳細に説明する。かかる排気浄化方法は、触媒に付着した煤（PM粒子）から水素を生成し、その水素を用いてNO_xを浄化する。即ち、内燃機関から排出される排気の温度が500°C以下のときに、次の反応式3及び/又は4



で表される水素生成反応を行なう。これより、500°C以下の温度でもPM粒子より水素が生成され、この水素を用いてNO_xを浄化し得る。

【0041】ここで、通常、NO_xの還元剤として排気中のHCやCO、更にH₂を使用する場合、リーン雰囲気では酸素が多く存在するため、これら還元剤はH₂OやCO₂になってしまふ。そのため、リーン雰囲気が大部分の運転条件（リーンバーンエンジンなど）の排気を浄化する場合においては、上記水素生成反応（式3及び4）が有効に利用できないという不具合があった。また、酸素過剰のリーン雰囲気では、触媒に付着したPMは水蒸気と水素生成反応（式3及び4）をほとんど行わない。

【0042】本発明の排気浄化触媒は、リッチ又はリーンの雰囲気に関係なく排気中に存在するPMを触媒表面

に付着させる。そして、このPMは、リッチ雰囲気のみならずリーン雰囲気でも、主にRhの作用により水素生成反応（式3及び4）に用いられ、水素が生成する。従って、リーン雰囲気でも生成した水素でNO_xを還元でき、NO_x浄化性能を向上できる。また、硫黄被毒されたNO_x吸着サイトのSO_xも水素によって還元できるため、NO_x吸着能を回復できるとともに新たな硫黄被毒を防止できる。これによってもNO_x浄化性能を向上できる。

【0043】具体的には、上記H₂生成触媒としては、少なくともロジウム（Rh）を担持した多孔質粒子の粉末と、鉄（Fe）、コバルト（Co）、マンガン（Mn）又はニッケル（Ni）、及びこれらの任意の組合せに係る金属とを含むものを用いる。このとき、上記Fe、Co、Mn及びNiなどの金属は上記多孔質粒子に担持されていることがよい。かかるH₂生成触媒を用いることにより、500°C以下の温度でPMとH₂Oから生成させたH₂により高いNO_x浄化性能を発現できる。また、後述するように、更にNO_x吸着材を用いると、リーンでNO_xを吸着するため、PMとH₂Oから生成したH₂とNO_xとの反応性が向上するので、NO_xの浄化反応を促進できる。更に、排気中のSO_xがNO_x吸着サイトと反応して触媒表面にSO_x吸着種やSO_x塩を形成することによりNO_x吸着能が消失してしまう（いわゆる硫黄被毒）場合があるが、上記生成させたH₂によりSO_xが還元されるため硫黄被毒を防止できる。更にまた、硫黄被毒を受けたNO_x吸着サイトもH₂により還元され、NO_x吸着能が復活し易い。

【0044】また、上記H₂生成触媒には、上記Fe、Co、Mn及びNiなどの金属が、Rhを1としたときに0.1～10の比率で含まれる。特に1～5であることがより好ましい。0.1より小さいとこれら金属による効果が現れず、Rhのみの場合と変わらない。一方、10を超えるとRhの活性が低下し、PMとRhの反応性が悪化してしまう。更に、上記Rhは、多孔質粒子120g当たり0.05～20gの範囲で担持されることが望ましい。Rhの担持量が0.05g/120gより少ないと耐久性が低下し易く、20g/120gより多いと上記効果が飽和するとともにコストの増大を招き易い。更に、Rhとともに白金（Pt）、パラジウム（Pd）及びイリジウム（Ir）などを担持することもでき、このときの担持量は、Rhとこれら金属との合計を上記範囲とすればよい。なお、上記多孔質粒子に担持されるPtは、多孔質粒子120g当たり0.1～10gの範囲であることが望ましい。Ptの担持量が0.1g/120gより少ないとHC、CO及びNO_xの浄化率が低下し易く、10g/120gより多くても効果が飽和するとともにコストの増大を招き易い。

【0045】また、上記多孔質粒子としては、例えば、アルミナ、シリカ、チタニア、ジルコニア、シリカーア

ルミナ及びゼオライトなどから適宜選択でき、1種を単独で使用したり、複数の種類を混合又は複合化して使用できる。但し、耐熱性が悪い、ZrはRhと相性が良いなどの理由から、Rh担持粉末にはアルミナ、ジルコニア又はジルコニアーアルミナを用いることが望ましい。更に、上記多孔質粒子の粒径は、0.1～20μmの範囲であることが好ましい。粒径が0.1μmより小さくRhの分散度が低下し、PMとH₂OからのH₂生成効果が十分に得られにくく、20μmより大きいとRh粉末同士が近接する確率が高くなり、結果としてRhの分散度が低下し、PMとH₂OによるH₂生成効果が十分に得られないことがある。

【0046】なお、上記多孔質粒子に更にNO_x吸着材を担持させることもでき、この場合は、NO_x吸着能を更に向上できる。かかるNO_x吸着剤としては、アルカリ金属、アルカリ土類金属又は希土類金属、及びこれらの任意の組合せに係る金属などを使用できる。具体的には、アルカリ金属としては、リチウム（Li）、ナトリウム（Na）、カリウム（K）及びセシウム（Cs）などが挙げられる。アルカリ土類金属としては、周期表2A族元素であるマグネシウム（Mg）、カルシウム（Ca）、ストロンチウム（Sr）、バリウム（Ba）などが挙げられる。希土類金属としては、ランタン（La）、セリウム（Ce）及びプラセオジム（Pr）などが挙げられる。また、このNO_x吸着材は、多孔質粒子120g当たり0.05～3.0モルの範囲で担持せることが望ましい。担持量が0.05モル/120gより少ないとNO_x浄化率が低下し易く、3.0モル/120gより多く担持しても効果が飽和し易い。更に、上記多孔質粒子にRh及びPtを担持させたときは、Rhと、Ni、Fe、Co、Mnなどの金属等の作用を充分引き出すために、Rh担持多孔質粒子（第1粉末）とPt担持多孔質粒子（第2粉末）を別々に製造し、その後これらを混合することがよい。この場合、第1粉末と第2粉末の混合比は、RhとPtの重量比換算で第1粉末：第2粉末=0.05:1～1:1の範囲が望ましい。また、第1粉末及び第2粉末がともに多孔質粒子としてアルミナを用いた場合は、アルミナの重量比換算で第1粉末：第2粉末=0.1:1～2:1の範囲が望ましい。これらの範囲から外れると、上記したRh及びPtの過不足の場合と同様の不具合が発生する場合がある。また、上記多孔質粒子に遷移金属を担持させたときは、更にMgを担持せることが望ましい。この助触媒を使用することにより、水素生成反応が促進され易いので有効である。

【0047】本発明では、上述の排気浄化触媒を用いて、排気中のパーティキュレート粒子及び窒素酸化物を浄化する排気浄化装置とすることができる。即ち、本発明の排気浄化装置は、内燃機関の排気煙道の上流側に上記水素生成触媒を配設し、その下流側に上記窒素酸化物

浄化触媒を配設して成る。このような構成とすることで、上記水素生成反応（式3及び4）を促進させる排気浄化装置となる。また、本発明の他の排気浄化装置は、内燃機関の排気煙道上に上記窒素酸化物浄化触媒の積層体を配設し、その上に上記水素生成触媒を被覆して成る。例えば、NO_x触媒を多層化し、その最上層にFe、Co、Mn又はNi、及びこれらの任意の組合せから成る金属を含むRh粉末を被覆することができる。

【0048】

【実施例】以下、本発明を実施例及び比較例により更に詳細に説明するが、本発明はこれら実施例に限定されるものではない。

【0049】以下の実施例1～3及び比較例1～3では、本発明の排気浄化装置、即ち、炭化水素（HC）生成触媒を用いた排気浄化装置について、性能評価試験を行った。

【0050】（実施例1）硝酸アルミニウムの水溶液に平均粒径0.5μmの超微粒アルミナを分散させて得た硝酸酸性水溶液に、気孔率60%、平均気孔径18μmであり、1平方インチ当たり約200セルの通気孔を有するコーチェライト製ハニカム型交互目詰めフィルタ2.5Lを浸した後、熱風乾燥一焼成工程を3回繰り返し、フィルタの気孔内壁にアルミナを分散担持させた。このときのアルミナの担持量は、フィルタ容積1L当たり約85gであった。また、このフィルタを、Pt濃度が約2.5%のジニトロジアンミンPt水溶液に浸し、熱風乾燥一焼成工程を2回繰り返し、フィルタの気孔内壁に分散担持させたアルミナにPtを担持させた。更に、このフィルタに無電解メッキを施し、フィルタ触媒1Aを得た。メッキ法は、Ptと還元剤を含むメッキ浴水溶液に上記ハニカムフィルタを浸し、Ptを析出させて得た。このときのPtの担持量は、フィルタ容積1L当たり約10gであった。

【0051】このフィルタ触媒1Aの前段に配置するHC及びSOFを吸着除去する機能を有するハニカム状モノリス材（ハニカム触媒1B）を次のようにして得た。含浸法によって比表面積約220m²/gのγアルミナを主成分とする活性アルミナにPtを2.5%担持させて得たPt/γアルミナ粉末を、比表面積約830m²/g、平均細孔径約3.2nmのポーラスシリカと、比表面積450m²/gでシリカアルミナ比約90のゼオライトβ、更に比表面積350m²/gでシリカアルミナ比約70のMFIゼオライトを重量比1:4:1で混合し、ベーマイト粉末とともに5:6:1の重量比で混合し、更に硝酸酸性アルミナゾルを1%加え、水と混合してスラリー液を得た。該スラリーを1平方インチ当たり400セルの通気孔を有するコーチェライトハニカム1.5Lに100g/Lコーティングし、乾燥、焼成の過程を経て、ハニカム状酸化触媒R1Bを得た。このハニカム状酸化触媒R1Bと、気孔率60%、平均気孔径18μmで、1平方インチ当たり約200セルの通気孔を有するコーチェライト製ハニカム型交互目詰めフィルタ2.5Lを直列に配置し、一つのコンバーターに組み込むことにより、比較例1になる排気浄化装置R1を得た。なお、この装置R1は、いわゆる従来の連続再生式トラップと類似の構成を有する。

1Aとを、それぞれ前段、後段に組み合せて、一つのコンバーターに組み込むことにより、排気浄化装置1を得た。

【0052】（実施例2）前段にハニカム触媒を設置せず、フィルタ触媒2Aのみとした以外は、実施例1と同様の操作を繰り返して、排気浄化装置2を得た。

【0053】（実施例3）気孔率60%、平均気孔径18μmであり、1平方インチ当たり約200セルの通気孔を有するコーチェライト製ハニカム型交互目詰めフィルタ1.25Lと、気孔率65%、平均気孔径32μmであり、1平方インチ当たり約200セルの通気孔を有するコーチェライト製ハニカム型交互目詰めフィルタ1.25Lとを用意し、実施例1とほぼ同様の操作を繰り返して、2つのフィルタ触媒3A₁及び3A₂を得た。これらのフィルタ触媒3A₁及び3A₂とハニカム触媒3Bを直列に配置して、排気浄化装置3を得た。即ち、これら触媒は、排気上流側から、ハニカム触媒3B—フィルタ触媒3A₂—フィルタ触媒3A₁の順に配置した。

【0054】（比較例1）含浸法によって比表面積約220m²/gのγアルミナを主成分とする活性アルミナにPtを2.5%担持させて得たPt/γアルミナ粉末を、ベーマイト粉末と10:2の重量比で混合し、更に硝酸酸性アルミナゾルを1%加え、水と混合してスラリー液を得た。該スラリーを1平方インチ当たり400セルの通気孔を有するコーチェライトハニカム1.5Lに100g/Lコーティングし、乾燥、焼成の過程を経て、ハニカム状酸化触媒R1Bを得た。このハニカム状酸化触媒R1Bと、気孔率60%、平均気孔径18μmで、1平方インチ当たり約200セルの通気孔を有するコーチェライト製ハニカム型交互目詰めフィルタ2.5Lを直列に配置し、一つのコンバーターに組み込むことにより、比較例1になる排気浄化装置R1を得た。なお、この装置R1は、いわゆる従来の連続再生式トラップと類似の構成を有する。

【0055】（比較例2）比較例1と同じPt/γアルミナ触媒のスラリーを、実施例1と同じコーチェライト製ハニカム型交互目詰めフィルタ2.5Lにコーティングし、熱風乾燥一焼成工程を4回繰り返すことによりフィルタの片側にPt/アルミナ触媒を担持させて、フィルタ触媒R2Aを得た。このときのPt/アルミナ触媒の担持量は、フィルタ容積1L当たり約100gであった。このフィルタ触媒R2Aのみで、排気浄化装置R2を得た。なお、この排気浄化装置R2は、実施例2の排気浄化装置2と比較して、フィルタ触媒の製法を変えたもの、即ち、フィルタ内壁表面にはPt/アルミナ触媒を担持せず、フィルタ外壁に触媒層を形成したものである。

【0056】（比較例3）比較例2と同じフィルタ触媒R2Aの前段に実施例1と同じハニカム触媒1Bを配置

させて、一つのコンバーターに組み込むことにより、排気浄化装置R3を得た。

【0057】<評価試験例>コモンレールシステムを備えた4気筒2.5Lの直噴型ディーゼルエンジンを設置したエンジンダイナモ装置を用いて、実施例及び比較例の排気浄化装置の性能評価試験を行った。なお、本評価装置は、触媒システム入口の排気温度を、エンジンの負荷、吸気絞り及びコモンレールシステムによるポスト噴射により制御できるものを用いた。また、排気浄化装置の性能評価法は、装置の入口温度を250°Cで2分保持し、次いで300°Cで3分保持し、更に350°Cで1分間保持するパターンを5時間繰り返す過渡性能評価法を用いた。なお、本評価試験では、スウェーデンクラス1軽油を用いた。

【0058】上記評価試験において、排気浄化装置1(実施例1)について、PM及びNOxの平均低減率を算出したところ、PM除去率は93%、NOx除去率は46%であった。また、初期に対する5時間運転後の圧力損失上昇は、25mmHgであった。同様に、排気浄化装置2(実施例2)に関しては、運転2時間における低減率は、PM除去率が90%、NOxが除去率55%であった。また、初期に対する4時間運転後の圧力損失上昇は、32mmHgであり、PM中のSOFによる触媒成分の被覆が起こり酸化性能が経時に低下したものと思われる。これより、排気浄化装置1のように、前段側でSOF分を除去することにより触媒の被覆を防止し、耐久性が高まることがわかる。また、排気浄化装置3(実施例3)に関しては、PM除去率が95%、NOx除去率が57%であった。また、初期に対する5時間運転後の圧力損失上昇は、18mmHgであった。これより、フィルタを分割した効果が発揮されていることがわかる。

【0059】一方、排気浄化装置R1(比較例1)に関しては、PM除去率が95%、NOx除去率が2%であり、NOx低減率が実施例に比べて低く、また、運転3時間後の圧力損失上昇が40mmHgを超えてしまいエンジン負荷が大きくなつたために、その時点で運転を取りやめた。また、排気浄化装置R2(比較例2)に関しては、PM除去率が92%、NOx除去率が8%であり、また、初期に対する運転3時間後の圧力損失上昇が40mmHgを超えてしまいエンジン負荷が大きくなつたために、その時点で運転を取りやめた。更に、排気浄化装置R3(比較例3)に関しては、PM除去率が92%、NOx除去率が11%であり、また、初期に対する4時間運転後の圧力損失上昇が40mmHgを超えてしまいエンジン負荷が大きくなつたために、その時点で運転を取りやめた。

【0060】また、排気浄化装置の性能評価条件を、入口温度を300°Cで5分保持し、更に400°Cで2分間保持するパターンにかえた場合、5時間運転後の排気淨

化装置1によるPM及びNOxの平均低減率は、PM除去率が91%、NOx除去率が16%となり、これより、高温排気条件では特にNOxの低減率が悪化することがわかる。本発明の排気浄化装置は、排気温度が30°C以下の条件で使用して効果が大きいので、排気温度の低い高効率の内燃機関の排気浄化に好適であることは明らかであるが、排気温度の高い内燃機関に対しても、配置位置を適宜選択することなどで温度条件を調整すれば対応可能となる。

【0061】以上のように、本発明の排気浄化装置を用いれば、200~350°C程度の比較的低排温条件の排気を高効率で浄化できるため、特別のエンジン制御法を用いなくても、容易にクリーン排気を実現できる。

【0062】次に、以下の実施例4~9及び比較例4~7では、本発明の排気浄化触媒、即ち、水素(H₂)生成触媒及び窒素酸化物(NOx)浄化触媒を含んで成る排気浄化触媒について、性能評価試験を行った。

【0063】(実施例4)硝酸Fe水溶液を活性アルミナ粉末(平均粒子径1μm)に含浸し、乾燥後空気中400°Cで1時間焼成して、Fe担持アルミナ粉末(粉末1)を得た。この粉末のFe濃度は2%であった。硝酸Rh水溶液を粉末1に含浸し、乾燥後、N₂中400°Cで1時間焼成して、Rh及びFe担持アルミナ粉末(粉末2)を得た。この粉末のRh濃度は2%であった(Fe/Rhはモル比で0.54)。ジアトロジアミンPt水溶液を活性アルミナ粉末に含浸し、乾燥後空気中400°Cで1時間焼成して、Pt担持アルミナ粉末(粉末3)を得た。この粉末のPt濃度は2%であった。

【0064】粉末3を70g、アルミナを70g、水140gを磁性ボールミルに投入し、混合粉碎してスラリ液を得た。このスラリ液をコーディライト質モノリス担体(1.3L、400セル)に付着して、空気流にてセル内の余剰のスラリを取り除き130°Cで乾燥した後、400°Cで1時間焼成し、コート層重量140g/L触媒担体(A)を得た。粉末2を70g、粉末3を70g、水140gを磁性ボールミルに投入し、混合粉碎してスラリ液を得た。このスラリ液を触媒担体(A)に付着して、空気流にてセル内の余剰のスラリを取り除き130°Cで乾燥した後、400°Cで1時間焼成し、総コート層重量280g/L触媒担体(B)を得た。触媒担体(B)に、酢酸Ba水溶液を酸化物換算で触媒1L当たり15g含浸担持させ、排気浄化触媒(C)を得た。

【0065】(実施例5)硝酸Feの代わりに硝酸Coを使用した以外は、実施例1と同様な操作を繰り返し、排気浄化触媒を得た(Co/Rhはモル比で0.57)。

【0066】(実施例6)硝酸Feの代わりに硝酸Niを使用した以外は、実施例1と同様な操作を繰り返し、排気浄化触媒を得た(Ni/Rhはモル比で0.57)。

【0067】(実施例7) 硝酸Feの代わりに硝酸Mnを使用した以外は、実施例1と同様な操作を繰り返し、排気浄化触媒を得た(Mn/Rhはモル比で0.53)。

【0068】(実施例8) 実施例1とほぼ同様な操作、即ち、粉末2を70g、粉末3を140g、アルミナを70g、水280gを磁性ボールミルに投入し、混合粉碎してスラリ液を得た。このスラリ液をコーディライト質モノリス担体(1.3L、400セル)に付着して、空気流にてセル内の余剰のスラリを取り除き130°Cで乾燥した後、400°Cで1時間焼成し、コート層重量280g/L触媒担体(B)を得た。触媒担体(B)に、酢酸Ba水溶液を酸化物換算で触媒1L当たり15g含浸担持させ、排気浄化触媒(C)を得た。

【0069】(実施例9) 活性アルミナの代わりに酸化ジルコニウムを使用した以外は、実施例1と同様な操作を繰り返し、排気浄化触媒を得た。

【0070】(比較例4) 硝酸Rh水溶液を活性アルミナ粉末(平均粒子径1μm)に含浸し、乾燥後、N₂中400°Cで1時間焼成して、Rh担持アルミナ粉末(粉末4)を得た。この粉末のRh濃度は2%であった。ジアトロジアミンPt水溶液を活性アルミナ粉末に含浸し、乾燥後空気中400°Cで1時間焼成して、Pt担持アルミナ粉末(粉末3)を得た。この粉末のPt濃度は2%であった。粉末3を70g、アルミナを70g、水140gを磁性ボールミルに投入し、混合粉碎してスラリ液を得た。このスラリ液をコーディライト質モノリス担体(1.3L、400セル)に付着して、空気流にてセル内の余剰のスラリを取り除き130°Cで乾燥した後、400°Cで1時間焼成し、コート層重量140g/L触媒担体(A)を得た。粉末2を70g、粉末3を70g、水140gを磁性ボールミルに投入し、混合粉碎

してスラリ液を得た。このスラリ液を触媒担体(A)に付着して、空気流にてセル内の余剰のスラリを取り除き130°Cで乾燥した後、400°Cで1時間焼成し、総コート層重量280g/L触媒担体(B)を得た。触媒担体(B)に、酢酸Ba水溶液を酸化物換算で触媒1L当たり15g含浸担持させ、排気浄化触媒(C)を得た。

【0071】(比較例5) 粉末1で、硝酸Feの濃度を0.2%にした以外は、実施例1と同様な操作を繰り返し、排気浄化触媒を得た。

【0072】(比較例6) 粉末1で、硝酸Feの濃度を4.0%にした以外は、実施例1と同様な操作を繰り返し、排気浄化触媒を得た。

【0073】(比較例7) 粉末1で、活性アルミナの粉末の平均粒子径を50μmにした以外は、実施例1と同様な操作を繰り返し、排気浄化触媒を得た。

【0074】<評価試験例>

・耐久方法

排気量4400ccのエンジンの排気系に排気浄化触媒を装着し、前段の触媒入口温度を700°Cとし、30時間運転した。

・評価方法

ディーゼルエンジンのエンジンの排気系に排気浄化触媒を装着し、触媒入口温度を300°Cとし、15分間運転した。ガソリンエンジンの排気系に排気浄化触媒を取り付け、A/F=5.0、入口温度300°Cとし、10分間運転した。なお、NO_x転化率は次の式

$$NO_x\text{転化率} = (1 - \text{触媒出口} NO_x\text{量} / \text{触媒入口} NO_x\text{量}) \times 100\%$$

により求めた。

【0075】

【表1】

	貴金属		元素		M/Rh(モル比)	Rh担持多孔質体積	多孔質体の粒子系
	Pt g/L	Rh g/L	M g/L				
実施例4	2.8	1.4	Fe	1.4	0.54	Al ₂ O ₃	1μm
実施例5	2.8	1.4	Co	1.4	0.51	Al ₂ O ₃	1μm
実施例6	2.8	1.4	Ni	1.4	0.51	Al ₂ O ₃	1μm
実施例7	2.8	1.4	Mn	1.4	0.53	Al ₂ O ₃	1μm
実施例8	2.8	1.4	Fe	1.4	0.54	Al ₂ O ₃	1μm
実施例9	2.8	1.4	Fe	1.4	0.54	ZrO ₂	1μm
比較例4	2.8	1.4	なし	0	0.54	Al ₂ O ₃	1μm
比較例5	2.8	1.4	Fe	0.14	0.054	Al ₂ O ₃	1μm
比較例6	2.8	1.4	Fe	28.0	10.8	Al ₂ O ₃	1μm
比較例7	2.8	1.4	Fe	1.4	0.54	Al ₂ O ₃	20μm

【0076】

【表2】

	転化率%
	NOx
実施例4	82
実施例5	80
実施例6	80
実施例7	77
実施例8	79
実施例9	80
比較例4	50
比較例5	60
比較例6	68
比較例7	68

【0077】表1及び表2に示すように、上記評価試験の結果、実施例4～9では、比較的低温な排気であってもNOx転化率が良好であることがわかる。一方、比較例4～7では、NOx転化率が悪いことがわかる。

【0078】以上、本発明を好適実施例及び比較例により詳細に説明したが、本発明はこれら実施例に限定されるものではなく、本発明の要旨の範囲内において種々の変形が可能である。例えば、本発明の触媒は、一体構造型担体に担持させて用いるのが望ましい。一体構造型担体としては、耐熱性材料からなるモノリス担体が望まし

く、例えばコーディライトなどのセラミック製や、フェライト系ステンレスなどの金属製の担体を使用できる。また、触媒を担体上に塗り分けることで、NOxとPMの排気浄化率を高めることができる。

【0079】

【発明の効果】以上説明してきたように、本発明によれば、PM中のC固体粒子（パーティキュレート粒子）を一旦炭化水素や水素に変換すること、触媒成分とPM粒子との接触（衝突）率を高めて該変換反応を促進させることとしたため、通常の燃焼条件の下で、特定の制御を必要とせずにNOxとPMを連続的に自己浄化することができる排気浄化方法、排気浄化触媒及び排気浄化装置を提供することができる。

【図面の簡単な説明】

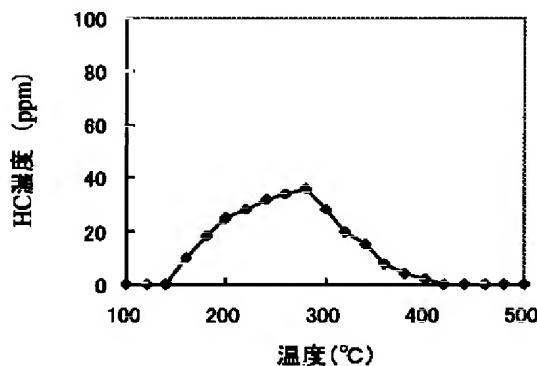
【図1】モデルガス評価試験によるCからのHC生成挙動を示すグラフである。

【図2】モデルガス評価試験によるNOx還元浄化特性を示すグラフである。

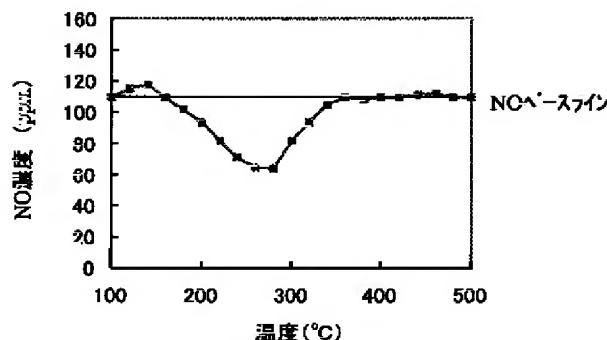
【図3】排気浄化装置の構成例を示す概略図である。

【図4】排気浄化装置の他の構成例を示す概略図である。

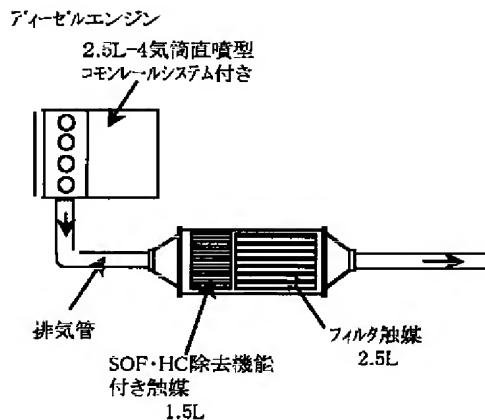
【図1】



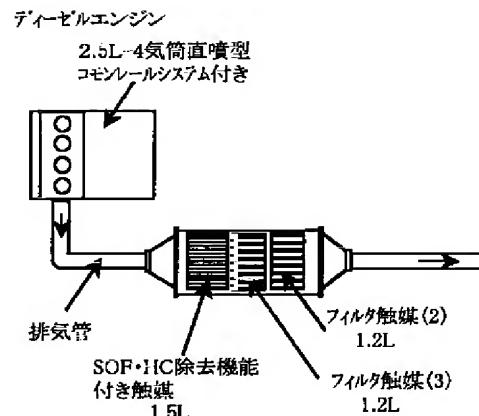
【図2】



【図3】



【図4】



フロントページの続き

(51) Int.Cl.7		識別記号	F I	(参考)
B 0 1 J	23/89		B 0 1 J	35/06 A 4 G 0 6 9
	29/74		F 0 1 N	3/02 3 0 1 E
	35/06			3/08 A
F 0 1 N	3/02	3 0 1		3/10
	3/08			3/24 C
	3/10			E
	3/24			3/28 3 0 1 C
	3/28	3 0 1	B 0 1 D	46/00 3 0 2
// B 0 1 D	46/00	3 0 2		46/42 B
	46/42			53/36 1 0 4 A
				Z A B
				1 0 4 B

(72)発明者 上條 元久
 神奈川県横浜市神奈川区宝町2番地 日産
 自動車株式会社内

F ターム(参考) 3G090 AA02 AA04
3G091 AA02 AA18 AB05 AB13 BA11
BA13 BA14 CA19 GA17 GA19
GA20 GB02Y GB03Y GB04Y
GB05W GB06W GB07W GB09Y
GB17X GB17Y HA08 HA18
4D019 AA01 BA05 BB03 BB06 BC07
BD01 CA01 CB04
4D048 AA06 AA14 AA17 AA18 BA03X
BA06Y BA07Y BA08X BA11X
BA12X BA28X BA30X BA31Y
BA33X BA36X BA37X BA38X
BA41X BB02 BB08 CC32
CC36 CC41 CC46 DA03 DA06
EA04
4D058 JA32 JB06 JB22 JB25 MA44
QA01 QA07 SA08 TA06
4G069 AA02 AA06 BA01A BA01B
BA02A BA04A BA06A BA06B
BA07A BA10A BC13B BC62A
BC62B BC66A BC66B BC67A
BC67B BC68A BC68B BC71A
BC71B BC72A BC75A BC75B
CA03 CA13 CA15 CA18 CC21
DA06 EA09 EA19 EB18X
EB18Y EC13X EC22Y EE06
FA01 FA02 FA03 FB13 FB21
FB23 FB30 FC08 ZA06A
ZA10A ZA10B ZA19A